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**FROM**

*Prof. Theodore Lyman.*

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*From October 1901 to December 1903.*

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# PROCEEDINGS

OF

## THE PHYSICAL SOCIETY

### OF LONDON.

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I. *Applications of Elastic Solids to Metrology.*  
*By C. CHREE, Sc.D., LL.D., F.R.S.\**

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#### *Fundamental Equations.*

§1. THE ordinary conception of a solid is apt to be that of a body whose shape and volume are variable only with temperature. Elastic changes in dimensions are necessarily small in most bodies of limited size, and they are often negligible even in exact metrological work. The present

\* Read May 10, 1901.

tendency is, however, to aim at an increasing accuracy in physical measurements, and it is open to doubt whether the steps taken in this direction are always guided by a sufficiently lively apprehension that solids are elastic, not rigid. The object of this paper is to exemplify the bearing of elasticity on physical measurements. Some of the points dealt with have met with previous recognition, but so far as my knowledge goes there has been no previous systematic treatment of them by an elastician. Many of the mathematical results used in this paper depend ultimately on a previous paper \*, published in 1892, in which I obtained expressions for the mean strains and for the change in total volume of any homogeneous elastic solid, acted on by any given system of forces throughout its mass or over its surface.

When the material is isotropic,  $E$  denotes Young's modulus,  $n$  the rigidity,  $\eta$  Poisson's ratio, and  $k(= \frac{1}{3}E/(1-2\eta))$  the bulk modulus.

When the material is aeolotropic but symmetrical with respect to 3 planes—supposed parallel to the coordinate planes—the suffixes 1, 2, 3 distinguish the directions parallel respectively to the axes of  $x$ ,  $y$ , and  $z$ . Thus  $E_1$  denotes Young's modulus for tension parallel to the  $x$ -axis, while  $\eta_{12}$  ( $=\eta_{21}$ ) is Poisson's ratio when the tension and the corresponding strain are parallel, the one to  $x$  the other to  $y$ . In all cases  $v$  represents the total volume of the solid,  $\rho$  its density,  $X, Y, Z$  the components of the bodily and  $F, G, H$  of the surface forces;  $\Delta$  is the dilatation,  $\alpha, \beta, \gamma$ , the elastic displacements, and  $e, f, g$  ( $=da/dx$ , &c.) the expansion strains. Mean values are distinguished by a horizontal line, e. g.  $\bar{e}$ , while  $\delta$  denotes (elastic) change in a dimension or in volume.

For an isotropic material the general formulæ obtained in the paper referred to above were of the types :

$$\begin{aligned} Ev\bar{g} &\equiv E \iiint \frac{d\gamma}{dz} dx dy dz \\ &= \iiint \{Zz - \eta(Xx + Yy)\} dx dy dz + \iint \{Hz - \eta(Fx + Gy)\} dS, \quad (1) \\ 3k\delta v &= \iiint (Xx + Yy + Zz) dx dy dz + \iint (Fx + Gy + Hz) dS; \quad . \quad (2) \end{aligned}$$

\* "Changes in the Dimensions of Elastic Solids." Camb. Phil. Trans. vol. xv. p. 313.

where the triple integrals are taken throughout the entire volume of the solid, the double integrals over its whole surface or surfaces. The coordinate axes are rectangular, the origin being at any convenient point in the solid. For aeolotropic solids there are analogous equations, for which reference may be made to the original paper.

*Suspended and Supported Solids.*

§ 2. Equation (2) gives the increment  $\delta v$  in the total volume, and thence the change in the mean density; while (1) gives the change in the mean length of a right cylinder. Thus, suppose a cylindrical bar of any form of section  $\sigma$  hung up by an end so that its axis—taken as axis of  $z$ —is vertical. We then have, measuring  $z$  downwards,

$$X=Y=0, \quad Z=g\rho,$$

where  $g$  is “gravity.” If we neglect the pressure of the surrounding medium,  $F, G, H$  vanish everywhere except at the top of the cylinder, where  $H$  answers to the tension of the string or support. We may avoid the necessity of considering this tension by simply supposing the origin of coordinates in the upper end of the bar; for then  $z$ , and so  $H z$ , vanishes everywhere where  $H$  itself does not vanish. If then  $\delta \bar{l}$  represent the mean change of the length  $l$  (*i. e.* the mean for all the vertical “fibres” constituting the bar), we have by (1)

$$\begin{aligned} \sigma \delta \bar{l} &\equiv \iint dx dy \left( \int_0^l \frac{dy}{dz} \right) dz \\ &= \frac{1}{E} \iiint g \rho z dx dy dz = \frac{1}{2E} g \rho l^2 \sigma, \end{aligned}$$

$$\text{whence} \quad \delta \bar{l}/l = g \rho l / 2E. \quad \dots \dots \dots (3)$$

Similarly from (2)

$$\delta v = (1/3k) \iiint g \rho z dx dy dz,$$

$$\text{whence} \quad \delta v/v = g \rho l / 6k \quad \dots \dots \dots (4)$$

Here  $\delta \bar{l}$  and  $\delta v$  represent how much the length and volume are greater than they would be in the absence of gravity.

If the bar instead of being suspended were supported in the same position, whether on a smooth plane or on a series

of points lying in one horizontal plane and exercising no friction, we should find in place of (3) and (4)

$$\delta \bar{l}/l = -gpl/2E, \quad . \quad . \quad . \quad . \quad . \quad (5)$$

$$\delta v/v = -gpl/6k. \quad . \quad . \quad . \quad . \quad . \quad (6)$$

By taking the arithmetic mean of the lengths or volumes of the bar when suspended and when supported, we clearly eliminate the action of gravity.

Even when the bar is kept in a uniform position, its length and volume are affected by any change in  $g$  such as follows change of place on the earth's surface. Again, as the elastic constants  $E$  and  $k$  will vary in general with the temperature, the changes in length and volume which accompany changes in temperature are in part—generally of course only in small part—of elastic, not of direct thermal origin.

### *Pressure of Surrounding Medium.*

§3. The expressions (3) to (6) neglect the pressure of the liquid or gaseous medium surrounding the solid. As this may vary, it is desirable to estimate its effect. So far as change of volume is concerned this is easily done as follows, for a body of any shape. The densities  $\rho$ ,  $\rho'$  of the solid and surrounding medium are supposed uniform. Take the case when the solid is suspended, and let  $p$  denote the pressure in the medium at the level of the centre of gravity of the solid. Take the origin of coordinates at the centre of gravity, and suppose that the axis of  $z$  is drawn vertically upwards. We know by elementary hydrostatics that the point of suspension must be in the same vertical as the centre of gravity; it thus lies on the axis of  $z$  at a height of, say,  $\zeta$  above the C.G. In the present case  $Z = -g\rho$ , thus by (2)

$$3k\delta v = -\iiint gpz dx dy dz + \iint (Fx + Gy + Hz) dS + \zeta \iint H dS', \quad . \quad (7)$$

where  $dS'$  is a portion of the infinitesimal surface where the suspending cord is attached, while  $dS$  is an element of the general surface of the body. By elementary statics,

$$\iint H dS' = \text{tension of string} = W - W',$$

where  $W$  is the weight of the solid *in vacuo*,  $W'$  the weight of the displaced medium. Again, if  $\lambda$ ,  $\mu$ ,  $\nu$  be direction-

cosines of the outwardly drawn normal at  $dS$ , we have

$$F/\lambda = G/\mu = H/\nu = -(p - gp'z),$$

and

$$\lambda x + \mu y + \nu z = \varpi,$$

where  $\varpi$  is the perpendicular from the C.G. on the tangent plane to the surface at  $x, y, z$ . Also, as the origin is at the C.G., the triple integral in (7) vanishes; thus we have

$$3k\delta v = -p \iint \varpi dS + gp' \iint \varpi z dS + \xi(W - W').$$

But

$$\iint \varpi dS = 3v,$$

and

$$\iint \varpi z dS = 0,$$

as follows from the consideration that the C.G. lies in the plane  $z=0$ .

Thus we have

$$\delta v = \frac{1}{3k} \{ (W - W')\xi - 3pv \}, \quad . . . \quad (8)$$

which may be put in the alternative form

$$\delta v/v = -\delta\rho/\rho = \{g(\rho - \rho')\xi - 3p\}/3k . . . \quad (8')$$

The change of volume, or mean density, may thus be regarded as composed of two distinct parts, the first representing the influence of the "apparent weight" of the solid in increasing the volume, the second the influence of the pressure of the surrounding medium in reducing the volume. The second part is the same as if the pressure in the medium were everywhere the same as at the level of the C.G. of the solid. This result, it will be noticed, is true irrespective of the shape or absolute size of the solid.

If the solid, instead of being suspended, had been supported on a horizontal plane, at a depth  $\xi'$  below the C.G., we should have got in place of (8) and (8'),  $p$  having the same meaning as before,

$$\delta v = -\{ (W - W')\xi' + 3pv \}/3k, \quad . . . \quad (9)$$

$$\delta v/v = -\delta\rho/\rho = -\{g(\rho - \rho')\xi' + 3p\}/3k . . . \quad (9')$$

The direct effect of the pressure exerted by the surrounding medium is the same in the two cases,

We can eliminate the influence of the support on the volume in three ways, by :

- i. Having the support at the level of the C.G. ;
- ii. Selecting for the surrounding medium a liquid of the same density as the solid ;
- iii. Taking the arithmetic mean of results from cases of suspension and of support in which  $\zeta' = \zeta$ .

§ 4. The results (8) and (9) have a special interest in connection with determinations of specific gravity. The ordinary method is to compare the weight of a body in air, after making allowance for the weight of air it displaces, with the loss of the apparent weight when it is weighed in water.

Now (8) and (9) call attention to the fact that the volume of the solid and so the weight of the medium it displaces depend both on the pressure of the surrounding medium and on the method of suspension. For instance, when a solid is weighed in water its volume, and so the volume of the water displaced, is diminished if it is sunk more deeply in the water, or if the atmospheric pressure on the surface of the water is increased. Again if, as is usual, the body rests on its base when weighed in the air, but is suspended by a wire when weighed in water, there is a change in its volume irrespective of any change in the pressure exerted by the medium.

We see from (8) and (9) that the influence of change of pressure on a given volume is independent of its shape, whereas the difference between the results in the suspended and supported positions increases as the vertical dimension. *Ceteris paribus*, the influence of pressure on total volume varies as the third power of the linear dimensions, whereas the influence of the mode of support varies as the fourth power. The latter influence thus tends to become relatively unimportant when the linear dimensions are very small.

As numerical examples, consider the effect of transfer from ordinary atmospheric pressure to a vacuum on the volume of (i.) steel, (ii.) brass, (iii.) lead. The elasticity of these materials has a pretty wide range, but if we assign to  $k$  the respective values\* (i.)  $18 \times 10^8$ , (ii.)  $10 \times 10^8$ , (iii.)  $2 \times 10^8$ ,

\* Cf. the tables in Lord Kelvin's article on Elasticity in the Enc. Brit.

in grammes weight per sq. cm., we shall obtain fairly representative results.

The supposed change in  $p$  is  $13.6 \times 76$ , or 1034, in grammes wt. per sq. cm., and we get the following approximate results :

$$\delta v/v = -\delta\rho/\rho = 58 \times 10^{-8} \text{ in (i.)}, = 103 \times 10^{-8} \text{ in (ii.)}, \\ = 517 \times 10^{-8} \text{ in (iii.)}.$$

As a second example, consider what would be the difference in the volume of one of the international standard kilograms of platinum iridium, if, instead of being supported on its base in air, it were suspended from the top. The form is approximately a right circular cylinder of height equal to the diameter, and the specific gravity is approximately 21.55; thus the height must be approximately 3.90 cm. The value of  $E$  is given by Benoit\* as probably about  $19.7 \times 10^8$  in grammes wt. per sq. cm., and if we suppose  $\eta = 1/3$  we have  $k = E$ . The difference in question is thus according to (8) and (9), neglecting the weight of the air displaced,

$$\delta v = W(\zeta + \zeta')/3k = 10^3 \times 3.9 \div (59 \times 10^8),$$

$$\text{or } \delta v = 66 \times 10^{-8} \text{ c.c. approx.,}$$

$$\delta\rho = -31 \times 10^{-8} \text{ approx.}$$

If the kilogram were in water the difference would be about 5 per cent. less than the above. If the kilogram were transferred from air at atmospheric pressure into a vacuum, the increment in volume would amount to about  $24 \times 10^{-6}$  c.c.

In the original work on the prototype kilograms by Marek† volumes are recorded to  $1 \times 10^{-5}$  c.c., so that in absolute strictness a standard pressure ought to be assigned at which a kilogram has its normal volume. Apparently, however, the last figure in Marek's results is treated as ornamental, the probable error affecting the previous significant figure. In Benoit's later work on the subject, while the observational volumes of the kilos are sometimes recorded to  $1 \times 10^{-8}$  c.c., the final statement of the accepted results gives two figures less.

\* *Trav. et Mém. Bureau International des Poids et Mesures*, tome vii. "Rapport" by Benoit, p. 27. [Benoit's value is given in connexion with the meter prototypes, which seem made of the same alloy as the kilograms.]

† *Trav. et Mém. du Bureau International*, tome iii.

We may thus conclude that for the highest degree of accuracy aimed at up to now, the laying down of a standard atmospheric pressure, or of a precise type of support, is unnecessary whether the kilo be in air or at a moderate depth in a liquid. If, however, a kilo were used at a great depth in a heavy liquid, or under a high gaseous pressure, the compressibility would require to be taken into account, and no very great increase in the accuracy aimed at by Marek and Benoit will be possible without making such an allowance. The fact that compressibility might come in was not overlooked by Marek, who gives (*l. c.* tome iii. p. D. 80) a formula equivalent to  $\delta v/v = -p/k$ , where  $p$  is the pressure at the level of the C.G. of the kilogram in a liquid in which it is being weighed. He gives, however, no explanation of how the result was reached, and it had probably no strict mathematical basis, but simply represented an assumption that the change of volume was the same as if the pressure over the surface of the kilogram had everywhere the mean value for the volume of liquid displaced. When the variation of pressure over the surface of the solid is relatively small, it is of course obvious *a priori* that an assumption of the kind cannot be much in error.

*Solid surrounded by Varying Medium.*

§ 5. The results (8) and (9) treat the density of the medium surrounding the solid as uniform. Strictly speaking, this can never be true. Ordinary liquids are much more compressible than solids; *e. g.* the values of  $k$  for water and for alcohol are of the orders  $20 \times 10^6$  and  $12 \times 10^6$  in grammes wt. per sq. cm. Thus increase in the depth to which a solid is immersed in a specific gravity experiment may be of most importance from its enhancing the density of the liquid. If  $p'$  and  $\rho'$  represent pressure and density in the liquid at depth  $z$ ,  $\Pi'$  the atmospheric pressure on  $z=0$ ,  $\rho_0'$  the density of the liquid if under zero-pressure, we have—neglecting  $(p'/k)^2$ —:

$$dp' = g\rho' dz,$$

$$\rho' = \rho_0'(1 + p'/k),$$

and when  $z=0$ ,

$$p' = \Pi'.$$



Proceeding by successive approximations, treating  $p'/k'$  as very small, we get

$$\rho' = \rho_0' \{ 1 + (\Pi + g\rho_0'z)/k' \}, \dots \dots \dots (10)$$

$$p' = \Pi' + g\rho_0'z \{ 1 + (\Pi'/k') + g\rho_0'z/(2k') \}. \dots (11)$$

Also for the weight of the liquid displaced by the solid we easily find

$$W' = g\rho_0'v \{ 1 + (\Pi' + g\rho_0'\xi)/k' \}, \dots \dots (12)$$

where  $v$  represents the volume of the *solid* as reduced by the pressure to which it is subjected, its density, however, being treated as uniform. The formulæ (8') and (9') assumed the density of the medium uniform. If, however, we assumed that  $\rho'$ , instead of being constant, varied according to the law (10), we should clearly add to the right-hand sides of (8') and (9') only terms involving the product  $(1/k) \times (1/k')$ , and unless  $k'/k$  were very small, the retention of these terms would be open to criticism. Under ordinary conditions we may utilize (8'), supposing the solid is suspended, and replace (12) by

$$W' = g\rho_0'v_0 \left\{ 1 + (\Pi' + g\rho_0'\xi) \left( \frac{1}{k'} - \frac{1}{k} \right) + g(\rho_0 - \rho_0')\xi/3k \right\}. (12')$$

Here  $v_0, \rho_0, \rho_0'$  refer to the ideal state of absolute freedom from pressure; but inside the square bracket the distinction between  $\rho$  and  $\rho_0$ , or  $\rho'$  and  $\rho_0'$  is negligible to the present degree of approximation. In general it would be more convenient in practice to have a standard atmospheric pressure  $\Pi$ . If  $v, \rho$ , and  $\rho'$  refer to this, then (12') becomes

$$W' = g\rho'v \left\{ 1 + (\Pi' - \Pi + g\rho'\xi) \left( \frac{1}{k'} - \frac{1}{k} \right) + g(\rho - \rho')\xi/3k \right\}. (13)$$

For the weight  $W''$  of air displaced in a weighing in air, we may take

$$W'' = g\rho''v \left\{ 1 + g \frac{(\rho - \rho'')\xi}{3k} + \frac{\Pi - \Pi''}{k} \right\}, \dots (14)$$

where  $v$  is the volume of the solid, unaffected by gravity, under standard pressure  $\Pi$ , while  $\Pi''$  is the atmospheric pressure, and  $\rho''$  the density of the air at the time of weighing.  $\Pi''$  and  $\rho''$  should be measured at the level of the C.G. of the body, which is supposed suspended. In general, the term  $-g\rho''\xi/3k$  inside the bracket in (14) might be neglected.

§ 6. When the variation in density of the liquid is taken into account, the integrals appearing in the expression for the change in volume of the solid would probably prove tractable only in particular cases. The case of a right circular cylinder or prism with its axis vertical may be treated as follows, the law of variation of the density with the depth being supposed continuous.

Let the origin of coordinates be at the upper end of the cylindrical axis,  $z$  being measured downwards; and let the density of the liquid follow the law  $\rho' = f(z)$ .

$$\text{Let} \quad \phi(z) \equiv \int_0^z f(z) dz, \quad . . . . . (15)$$

$$z\chi(z) \equiv \int_0^z \phi(z) dz. \quad . . . . . (16)$$

If the pressure be  $\Pi$  at  $z=0$ , then at depth  $z$  it is given by

$$p = \Pi + g\phi(z). \quad . . . . . (17)$$

For the change in the volume of the cylinder we have by (2)

$$3k\delta v = \iiint g\rho z dx dy dz - \iint (\lambda x + \mu y) p dS - \iint l p dx dy,$$

where  $l$  is the length of the cylinder,  $\lambda, \mu, 0$  the direction-cosines of the outwardly drawn normal to the cylindrical surface. The first double integral is taken over the cylindrical surface (or vertical faces, if the body is prismatic), the second double integral over the lower face  $z=l$ .

If now  $\varpi$  be the perpendicular drawn from the axis of the cylinder on the tangent at  $(x, y)$  to the horizontal section, we have

$$(\lambda x + \mu y) dS = (\varpi ds) dz,$$

where  $ds$  is an element of the perimeter of the cross section.

Also

$$\int \varpi ds = 2\sigma,$$

where  $\sigma$  is the area of the cross section;

and over the lower face

$$\iint l p dx dy = l \{ \Pi + g\phi(l) \} \sigma.$$

Thus we obtain

$$3k\delta v = g\rho(l/2)v - 2v\{\Pi + g\chi(l)\} - v\{\Pi + g\phi(l)\},$$

$$\text{or} \quad \delta v/v = \{g\rho(l/2) - g(\phi(l) + 2\chi(l)) - 3\Pi\}/3k. \quad (18)$$

This is true for all cases of continuous variation of density with the depth. In the particular case dealt with in § 5, where the change of density arises from the compressibility, we have

$$f(z) \equiv \rho_0' \{1 + (\Pi + g\rho_0'z)/k'\}.$$

$$\text{Thus} \quad \phi(z) = \rho_0' \{z(1 + \Pi/k') + \frac{1}{2}g\rho_0'z^2/k'\},$$

$$\chi(z) = \rho_0' \{\frac{1}{2}z(1 + \Pi/k') + \frac{1}{6}g\rho_0'z^3/k'\};$$

and after reduction we have

$$\delta v/v = \left\{ g\rho \frac{l}{2} - 3\Pi - g\rho_0'l \left( 2 + 2\frac{\Pi}{k'} + \frac{5}{6}g\rho_0' \frac{l}{k'} \right) \right\} / 3k. \quad (19)$$

Treating as negligible powers of  $\Pi/k'$  and  $g\rho_0'l/k'$  above the first, we can put this in the form

$$\delta v/v = \frac{1}{3k} \left[ g\rho \frac{l}{2} - g\rho_0' \frac{l}{2} \left( 1 + \frac{g\rho_0'l}{6k'} \right) \left( 1 + \frac{\Pi}{k'} + \frac{g\rho_0'l}{2k'} \right) - 3 \left\{ \Pi + \frac{g\rho_0'l}{2} \left( 1 + \frac{\Pi}{k'} + \frac{g\rho_0'l}{3k'} \right) \right\} \right].$$

But we have

$g\rho v = W$ , the weight of the solid,

$g\rho_0'v \left( 1 + \frac{\Pi}{k'} + \frac{g\rho_0'l}{2k'} \right) = W'$ , the weight of the liquid displaced,

$l/2 = \zeta$ , the depth of the C.G. of the solid,

$\frac{l}{2} \left( 1 + \frac{g\rho_0'l}{6k'} \right) = \zeta'$ , " " " " liquid displaced,

$\Pi + g\rho_0' \frac{l}{2} \left( 1 + \frac{\Pi}{k'} + \frac{g\rho_0'l}{3k'} \right) = \bar{p}$ , the mean value of the pressure between  $z=0$  and  $z=l$ .

Thus (19) is equivalent to

$$\delta v = (W\zeta - W'\zeta' - 3\bar{p}v)/3k. \quad (20)$$

§ 7. As an example of discontinuous variation of pressure, take the case of a cylinder or prism supported on its base

$z=0$ , surrounded to the height  $z=l_1$  by a liquid of density  $\rho'$ , and throughout the remainder  $l_2$  of its height by a liquid of density  $\rho''$ . If  $\Pi$  be the pressure in the liquid when  $z=0$ , then the pressure elsewhere is given by

$$p = \Pi - g\rho'z \text{ between } z=0 \text{ and } z=l_1,$$

$$p = \Pi - g\rho'l_1 - g\rho''(z-l_1) \text{ between } z=l_1 \text{ and } z=l_2.$$

Employing these values we easily find from (2) for the change in volume of the solid

$$\delta v/v = - \left\{ g\rho \frac{l_1+l_2}{2} + 3\Pi - 2g(\rho'l_1 + \rho''l_2) - g(\rho' - \rho'')l_1l_2/(l_1+l_2) \right\} / 3k. \quad (21)$$

For given values of  $l_1$ ,  $l_2$ ,  $\rho_1$ , and  $\rho_2$ , the reduction in the volume is least when—as is necessary for stable equilibrium—the heavier liquid is at the bottom.

### *Aeolotropic Solids.*

§ 8. As an example of an aeolotropic solid, take the case of a right prism or cylinder of density  $\rho$ , whose shape is symmetrical with respect to three planes of elastic symmetry, suspended with its axis vertical in a homogeneous liquid of density  $\rho'$ . In this species of material the general formula for the elastic change of volume is in place of (2) \*

$$\begin{aligned} \delta v = & \iiint \left\{ (1-\eta_{12}-\eta_{13})(Xx/E_1) + (1-\eta_{21}-\eta_{23})(Yy/E_2) \right. \\ & \left. + (1-\eta_{31}-\eta_{32})(Zz/E_3) \right\} dx dy dz \\ & + \iint \left\{ (1-\eta_{12}-\eta_{13})(Fx/E_1) + (1-\eta_{21}-\eta_{23})(Gy/E_2) \right. \\ & \left. + (1-\eta_{31}-\eta_{32})(Hz/E_3) \right\} dS. \quad . \quad . \quad . \quad (22) \end{aligned}$$

Noticing that the modulus  $k$  of resistance to compression under uniform surface-pressure is given by

$$1/k = (1-\eta_{12}-\eta_{13})E_1^{-1} + (1-\eta_{21}-\eta_{23})E_2^{-1} + (1-\eta_{31}-\eta_{32})E_3^{-1},$$

we find without much difficulty

$$\delta v/v = g(\rho - \rho') (1 - \eta_{31} - \eta_{32})(\zeta/E_3) - p/k, \quad . \quad (23)$$

where  $\zeta$  is the depth of the C.G. of the solid below the point of suspension, and  $p$  the pressure at this depth in the liquid.

If the cylinder were supported on its base we should get in place of (23)

$$\delta v/v = -g(\rho - \rho')(1 - \eta_{31} - \eta_{32})(\zeta'/E_3) - p/k, \quad . \quad . \quad (24)$$

where  $\zeta'$  is the height of the C.G. above the support,  $p$  having the same signification as in (23).

The last terms in (23) and (24) are the same as if the solid were subjected to a uniform pressure  $p$ ; they are independent of the orientation of the axes of elasticity. The first terms, however, representing the influence of the apparent weight, depend on which of the three principal axes of elasticity is vertical.

If the body were a cube of side  $2a$ , supported in turns with the three principal axes vertical, the corresponding changes  $\delta v_1$ ,  $\delta v_2$ ,  $\delta v_3$  in the volume are connected by the elegant relation

$$\delta v_1 + \delta v_2 + \delta v_3 = -\{(W - W')a + 3pv\}/k, \quad . \quad . \quad (25)$$

where  $W$  is the weight of the cube,  $W'$  the weight of the liquid displaced.

The formulæ (23), (24), (25) apply equally whether the surrounding medium be a liquid or a gas, but in the latter case  $\rho'/\rho$ , or  $W'/W$ , would usually be negligible. Supposing, for instance, a cylinder to be suspended first in air then in a liquid of density  $\rho'$ , the barometer remaining steady, the relative increment  $\delta\rho$  in its density in the latter case would be given by

$$\delta\rho = g\rho\rho'\{(1 - \eta_{31} - \eta_{32})(\zeta/E_3) + \zeta'/k\}. \quad . \quad . \quad (26)$$

Here the density of the air is neglected, the axis of  $z$  is supposed vertical,  $\zeta$  is the depth of the C.G. of the solid below the point of suspension, and  $\zeta'$  its depth below the surface of the liquid.

#### *Cylinder suspended from the rim.*

§ 9. The formulæ (8) and (9) apply whatever be the shape of the body; thus the change in volume of a suspended or supported solid is always ascertainable, neglecting variability in the surrounding medium. Changes of linear dimensions are, however, less manageable. As we shall see presently, we can obtain a complete solution when a right cylinder has its

axis or a rectangular prism one of its sides vertical; so that in that case we can do better than use the formula (1). In many cases probably it would be difficult to make much even of (1). The following, however, is a case where it applies satisfactorily.

An isotropic right circular cylinder of density  $\rho$ , radius  $a$ , and height  $h$ , is suspended by a point in its rim, in a liquid of density  $\rho'$ , to find the elastic change in its volume.

Take the origin of coordinates at the centre of the upper face, the axis of  $z$  along the axis of the cylinder, and the plane of  $xz$  to contain the point of suspension  $(-a, 0, 0)$ . As the C.G. must lie on the vertical through the point of suspension, the axis of the cylinder must be inclined to the vertical at the angle  $\alpha$  where

$$\alpha = \tan^{-1}(2a/h). \quad (27)$$

The data required as to the components of the fluid pressures are as follows,  $\Pi$  denoting the pressure in the liquid at the centre of the upper face:—

<i>Surface.</i>	<i>Values of Specified Components.</i>
Upper plane face, $z=0$ ,	$F=G=0$ ,
Lower „ „ $z=h$ ,	„ „ $H = -\{\Pi + g\rho'(h \cos \alpha + x \sin \alpha)\}$ ,
Cylindrical surface	$H=0$ , $F/x=G/y = -a^{-1}\{\Pi + g\rho'(z \cos \alpha + x \sin \alpha)\}$ .

Throughout the volume  $X=g\rho \sin \alpha$ ,  $Y=0$ ,  $Z=g\rho \cos \alpha$ .

At the point of suspension  $z=0$ ,  $x=-a$ , and the component of the tension of the supporting string parallel to  $x$  is given by

$$\iint F dS = -\pi(\rho - \rho')a^2 h g \sin \alpha.$$

It is unnecessary to reproduce the calculation, which presents few difficulties. The final result may be put in the form

$$\delta h/h = (1/E) \{g(\rho - \rho')(\frac{1}{2}h \cos \alpha - \eta a \sin \alpha) - (1 - 2\eta)p\}, \quad (28)$$

where  $p$  is the pressure in the liquid at the depth of the centre of gravity of the cylinder. An alternative form, see (27), is

$$\delta h/h = (1/E) \{g(\rho - \rho') \frac{(h/2)^2 - \eta a^2}{\{(h/2)^2 + a^2\}^{\frac{1}{2}}} - (1 - 2\eta)p\}. \quad (28')$$

The direct influence of the support on the length thus vanishes if

$$\eta = (h/2a)^2.$$

On the theory of uniconstant isotropy  $\eta=1/4$ ; in a material for which this held, the above relation would become

$$h=a,$$

or the height would be equal to half the diameter.

If in (28') we suppose  $a/h$  vanishingly small, we obtain the correct result for the elastic stretching of a cylinder whose axis is vertical; while if we suppose  $h/a$  negligible, we get the mean elastic reduction in thickness of a thin disk supported from a point in its rim with its plane vertical.

*Solid Cylinder or Prism with axis vertical;  
Complete Solution.*

§ 10. As already stated, the case of a right cylinder or prism with the axis vertical can be solved completely.

Take the origin at the C.G., the axis of  $z$  being drawn vertically upwards, and let  $h$  denote the length of the axis or vertical edges. If  $\rho'$  be the density of the liquid, and  $p$  the pressure in the liquid at the level of the C.G., then the pressure at a height  $z$  is  $p - g\rho'z$ .

The body stress equations are

$$\left. \begin{aligned} \frac{\widehat{xx}}{dx} + \frac{\widehat{xy}}{dy} + \frac{\widehat{xz}}{dz} &= \frac{\widehat{xy}}{dx} + \frac{\widehat{yy}}{dy} + \frac{\widehat{yz}}{dz} = 0, \\ \frac{\widehat{xz}}{dx} + \frac{\widehat{yz}}{dy} + \frac{\widehat{zz}}{dz} &= g\rho. \end{aligned} \right\} \dots (29)$$

On the curved surface, or vertical sides, the direction cosines of the normal being as before  $\lambda, \mu, 0$ , we must have

$$(\lambda\widehat{xx} + \mu\widehat{xy})/\lambda = (\lambda\widehat{xy} + \mu\widehat{yy})/\mu = -(p - g\rho'z). \dots (30)$$

The conditions over the flat ends vary according to the special circumstances.

The equations (29) and (30) are satisfied by

$$\left. \begin{aligned} \widehat{xx} &= \widehat{yy} = -(p - g\rho'z), \\ \widehat{zz} &= g\rho z + C \text{ (a constant)}, \\ \widehat{xz} &= \widehat{yz} = 0. \end{aligned} \right\} \dots (31)$$

As to the conditions over the ends:—

(i.) If the cylinder has its upper end held—whether sus-

pended or pushed down—the base being freely exposed to the liquid,

$$\gamma = 0 \text{ when } z = h/2, \text{ for, say, } x = y = 0,$$

$$\widehat{zz} = -(p + g\rho'h/2) \text{ when } z = -h/2.$$

The latter condition gives

$$C = -p + g(\rho - \rho')h/2;$$

and the complete solution will be found to be

$$\left. \begin{aligned} \widehat{xx} = \widehat{yy} &= -(p - g\rho'z), \\ \widehat{zz} &= -p + g(\rho - \rho')\frac{h}{2} + g\rho z, \\ \widehat{xy} = \widehat{xz} = \widehat{yz} &= 0; \end{aligned} \right\} \dots \dots \dots (32)$$

$$\left. \begin{aligned} \alpha/x = \beta/y &= -(1/E) \left[ (1 - 2\eta)p + \eta g(\rho - \rho')\frac{h}{2} + g z \{ \eta\rho - (1 - \eta)\rho' \} \right], \\ \gamma &= -\frac{(z - h/2)}{E} \left[ (1 - 2\eta)p - \frac{g h}{4} \{ 3\rho - 2(1 + \eta)\rho' \} - \frac{1}{2} g z (\rho - 2\eta\rho') \right] \\ &\quad + \frac{1}{2} \frac{g}{E} (x^2 + y^2) \{ \eta\rho - (1 - \eta)\rho' \}. \end{aligned} \right\} (33)$$

The force per unit area exerted at the top of the cylinder or prism, *i. e.* the value of  $\widehat{zz}$  when  $z = h/2$ , is

$$g\rho h - (p + g\rho'h/2).$$

It is thus—as follows from ordinary Hydrostatics—a pull or a push according as the weight of the cylinder is greater or less than the pressure exerted by the liquid on the base.

The elastic increment in the height is deducible from (33), whence

$$\delta h/h = g(\rho - \rho')(h/2E) - (1 - 2\eta)p/E. \dots \dots (34)$$

(ii.) If the cylinder or prism is supported on its base, the upper surface being freely exposed to the liquid, the terminal conditions are

$$\gamma = 0 \text{ when } z = -h/2, \text{ for, say, } x = y = 0,$$

$$\widehat{zz} = -(p - g\rho'h/2) \text{ when } z = +h/2.$$



The solution will be found to be

$$\left. \begin{aligned} \widehat{xx} = \widehat{yy} &= -(p - g\rho'z), \\ \widehat{zz} &= -p - g(\rho - \rho')\frac{h}{2} + g\rho z; \end{aligned} \right\} \dots \dots (35)$$

$$\left. \begin{aligned} x/x = y/y &= -(1/E) \left[ (1-2\eta)p - \eta g(\rho - \rho')\frac{h}{2} + gz\{\eta\rho - (1-\eta)\rho'\} \right], \\ \gamma &= -\frac{(z+h/2)}{E} \left[ (1-2\eta)p + \frac{gh}{4}\{3\rho - 2(1+\eta)\rho'\} - \frac{1}{2}gz(\rho - 2\eta\rho') \right] \\ &\quad + \frac{1}{2}\frac{g}{E}(x^2 + y^2)\{\eta\rho - (1-\eta)\rho'\}. \end{aligned} \right\} (36)$$

The pressure per unit area exerted at the base of the cylinder or prism, *i. e.* the value of  $-\widehat{zz}$  when  $z = -h/2$ , is

$$g\rho h + (p - g\rho'h/2).$$

The total pressure thus equals, as it ought, the weight of the solid plus the total pressure exerted by the liquid on the upper flat surface.

Our assumption that the vertical displacement  $\gamma$  vanishes when  $x=y=0$  over the upper surface  $z=h/2$  in case (i.), and over the lower surface  $z=-h/2$  in case (ii.) is really arbitrary. The making a displacement vanish at a particular point is merely equivalent to introducing a constant into the expression, and this is without effect on the strains or stresses. Case (i.) includes several sub-cases. Thus if  $\rho' = \rho$  it applies to a cylinder or prism floating wholly immersed in a liquid of equal density. The stress  $\widehat{zz}$  at the upper face then becomes a pressure and equals, as it ought, the pressure  $p - g\rho'h/2$  at the same depth in the liquid. If  $\rho$  exceed  $\rho'$  we have the case of a cylinder supported from above, with the whole, or a portion  $h$ , of its length immersed. Supposing the portion  $h$  alone immersed, the atmospheric pressure on the liquid surface being  $\Pi$ , the value of  $\widehat{zz}$  over the surface  $z = +h/2$  becomes

$$g(\rho - \rho')h - \Pi.$$

It is thus a pull or a push according as

$$g(\rho - \rho')h > \text{ or } < \Pi;$$

*i. e.* according as the length of the immersed portion of the cylinder is greater or less than the barometric height as given by a barometer containing a liquid whose density is  $\rho - \rho'$ .

If the whole of the cylinder be immersed, then the liquid must not have access to any part of the upper surface, otherwise the stress could not differ from the liquid pressure at that depth.

If  $\rho$  be less than  $\rho'$  the cylinder may be held down either partly immersed, or fully immersed but with its upper surface not exposed to the liquid, or it may float with a length  $h'$  emergent.

In the latter event  $\widehat{zz}$  over  $z = h/2$  must represent the pressure exerted on its base by a cylinder of density  $\rho$  and height  $h'$ , whose upper surface is exposed to atmospheric pressure. Thus, neglecting the variation of atmospheric pressure throughout the height  $h'$ , we have

$$-g\rho h' = g\rho h - g\rho' h,$$

or

$$\rho(h + h') = \rho' h,$$

in accordance with elementary Statics.

Case (ii.) in like manner includes various sub-cases. The first thing to notice is that unless  $\rho = \rho'$  the solution assumes that the liquid cannot reach any part of the base; otherwise  $\widehat{zz}$  could not have the value assigned to it when  $z = -h/2$ . This explains why the solution does not in itself introduce the restriction  $\rho > \rho'$ . In practice, a solid lighter than a liquid in which it is immersed almost invariably rises to the surface of the liquid, but if the lower surface of the solid and the bottom of the vessel holding the liquid be both perfectly smooth, this need not happen. Usually liquid would force its way under the base, so that in practice the solution would apply only to a cylinder cemented to the bottom or projecting up through it like a pile. When a cylinder or prism rests on, or is supported from, a series of isolated supports, the stress  $\widehat{zz}$  is not uniform over the cross section, and the previous solutions do not strictly apply. If, however, the height  $h$  be great compared to the largest horizontal dimension, the

solutions will be very approximately true except in the immediate neighbourhood of the supports.

*Flask containing Liquid.*

§ 11. In obtaining (8) and (9) we tacitly assumed that there were no cavities in the solid, or that the liquid pressure was the same at all points in the same horizontal plane. When cavities exist complications arise. It is always possible to find the change in the volume of the *material* itself; but in the case, for example, of a flask containing liquid, what is of most interest is not the change in volume of the material but the change in the volume contained by the inner surface. The change in volume of the material of the flask may be obtained, at least very approximately, as follows:—Take the origin in the inner surface of the base of the flask, whose bottom is supposed a plane surface  $z = -t$ ; take the axis of  $z$  vertically upwards, and let  $h$  be the height of the liquid surface above  $z = 0$ . The material being supposed of density  $\rho$ , the change in its volume is given by (1). Throughout the volume

$$X=Y=0, \quad Z=-g\rho;$$

and supposing  $\rho'$  the density of the liquid, we have, over the inner surface  $S$ ,

$$F/\lambda = G/\mu = H/\nu = g\rho'(h-z),$$

where  $\lambda, \mu, \nu$  are direction-cosines of the normal (above the level of the liquid  $F=G=H=0$ , neglecting the atmospheric pressure). Over the outer surface no force is supposed to act, except over the lower surface  $S'$  of the base where  $H$  alone exists. Thus we have

$$3k\delta v = -\iiint g\rho z dx dy dz + \iint g\rho'(h-z)(\lambda x + \mu y + \nu z)dS + \iint (-t)H dS'.$$

The values of the several integrals are as follows:—

$$-\iiint g\rho z dx dy dz = -g\rho\bar{z}v,$$

$$\iint g\rho'(h-z)(\lambda x + \mu y + \nu z)dS = g\rho'r'(3h - 4z').$$

$$\iint (-t)H dS' = -gt(\rho v + \rho'r').$$

Here  $v$  is the volume of the material of the flask,  $\bar{z}$  the height of its C.G. above the upper surface of its bottom;  $v'$  similarly is the volume of the liquid,  $\bar{z}'$  the height of its C.G.

In all we have

$$\delta v = -g\rho v(\bar{z} + t)/(3k) + g\rho'v'(3h - 4\bar{z}' - t)/3k. \quad (37)$$

This expression becomes neater if instead of  $\bar{z}$ ,  $\bar{z}'$ , and  $h$  we use  $\xi$ ,  $\xi'$ , and  $H$ , the heights respectively of the two C.G.'s and the liquid surface above the lower surface of the bottom of the flask (*i. e.*  $\xi = \bar{z} + t$ , &c.). We then get

$$\delta v = -g\rho v\xi/(3k) + g\rho'v'(3H - 4\xi')/3k, \quad (37')$$

or

$$\delta v = -W\xi/(3k) + W'(3H - 4\xi')/3k, \quad (37'')$$

where  $W$  and  $W'$  are the weights of the flask and of the contained liquid. We have neglected the influence of atmospheric pressure, which is the same as in (8) or (9). For comparative results we may also neglect the influence of the flask's own weight, supposing it supported in an invariable way, and confine our attention to the effect of the weight of the liquid, as practically the only variable. For this we have

$$\delta v = W'(3H - 4\xi')/3k. \quad (38)$$

For given values of  $W'$ ,  $H$ ,  $\xi'$ , and  $k$ , the change in the total volume of the flask's material is the same for all values of that volume. A thin-walled flask suffers exactly the same change of volume as a thick-walled flask. This seems rather paradoxical at first sight. It simply means, however, that the mean expansion per unit of volume varies inversely as the whole volume. The thin-walled flask, owing to its smaller volume, has the larger expansion per unit of volume, and so the larger internal strains and stresses.

The change  $\delta v$  refers to the whole flask; but in such a case as that of a litre or 500 c.c. flask filled up to the mark,  $\delta v$  would practically apply to the portion below the mark.

If the flask, instead of being supported, floated immersed to a depth  $H'$  in the liquid, we should obtain in place of (37''), neglecting atmospheric pressure as before,

$$\delta v = -W\xi/3k - W''(3H' - 4\xi'')/3k, \quad (39)$$

where  $W''$  is the weight of the liquid displaced,  $\zeta''$  the height of its C.G. above the base of the flask.

Ordinarily, internal liquid pressure will tend to increase and external liquid pressure to diminish the volume of the walls of the flask. If, however,  $\zeta'$  exceed  $3H/4$ , and  $\zeta''$  exceed  $3H'/4$ , the reverse will be the case.

If the inner surface of the flask be cylindrical or cup-shaped,  $\zeta'$  will be less than  $3H/4$ . The two would become equal if the inner surface were a cone vertex downwards, and  $\zeta'$  would exceed  $3H/4$  for certain cusped forms of surfaces.

Thus, theoretically, a flask whose inner surface was a cone, of any solid angle, vertex downwards, would have the curious property that the volume of the material would be unaffected by the pressure of any liquid it might contain.

*Hollow Cylinder containing or surrounded by Liquid.*

§ 12. As already stated, we cannot in general determine the effect on the internal capacity of a flask due to the pressure of contained liquid. We can, however, obtain this information when the walls of the flask are coaxial right circular cylinders, the common axis being vertical. Take the origin at the lowest point of the axis, and employ cylindrical coordinates  $r, \phi, z$ . For generality suppose that gravity acts, while pressures  $\Pi + Cz$  and  $\Pi' + C'z$  act respectively on the outer surface  $r=a$  and the inner surface  $r=a'$ . These are typical of pressures exerted by surrounding or contained liquids of uniform density. Employing a method of solution given in the Camb. Phil. Trans. vol. xiv. pp. 328 *et seq.*, I find for the values of the stresses

$$\left. \begin{aligned} \widehat{rr} &= -\{\Pi a^2 - \Pi' a'^2 + (\Pi' - \Pi)(aa'/r)^2 + (Ca^2 - C'a'^2)z \\ &\quad + (C' - C)z(aa'/r)^2\}/(a^2 - a'^2), \\ \widehat{\phi\phi} &= -\{\Pi a^2 - \Pi' a'^2 + (\Pi - \Pi')(aa'/r)^2 + (Ca^2 - C'a'^2)z \\ &\quad + (C - C')z(aa'/r)^2\}/(a^2 - a'^2), \\ \widehat{zz} &= -Z - gpl + gpz, \\ \widehat{\phi r} = \widehat{rz} = \widehat{\phi z} &= 0; \end{aligned} \right\} \quad (40)$$

where  $Z$  is a uniformly distributed longitudinal stress supposed to act at the height  $z=l$ . The corresponding values of the displacements,  $u$  along  $r$  and  $w$  parallel to  $z$ , are

$$\left. \begin{aligned} u &= (r/E) \left\{ \eta(Z + g\rho l) - (1-\eta) \frac{\Pi a^2 - \Pi' a'^2}{a^2 - a'^2} \right\} - \frac{(\Pi - \Pi') a^2 a'^2 / r}{2n(a^2 - a'^2)} \\ &\quad - \frac{\eta}{E} g\rho r z - \frac{C a^2 - C' a'^2}{E(a^2 - a'^2)} (1-\eta) r z - \frac{(C - C') a^2 a'^2 z / r}{2n(a^2 - a'^2)}, \\ w &= (z/E) \left\{ -Z - g\rho l + 2\eta \frac{\Pi a^2 - \Pi' a'^2}{a^2 - a'^2} \right\} + \frac{1}{2} \frac{g\rho}{E} (z^2 + \eta r^2) \\ &\quad + \frac{C a^2 - C' a'^2}{2E(a^2 - a'^2)} \{ (1-\eta) r^2 + 2\eta z^2 \} + \frac{(C - C') a^2 a'^2}{2n(a^2 - a'^2)} \log(r/r_1), \end{aligned} \right\} \quad (41)$$

where  $r_1$  is a constant, which can be determined so as to make  $w$  vanish at any assigned value of  $r$  when  $z=0$ .

The general form of the solution, when  $\Pi$  and  $\Pi'$ ,  $C$  and  $C'$  are unequal, implies that the external and internal liquids are of unequal densities and do not communicate at all, or only at a level where the pressures are equal. Thus, in general, we must suppose that the cylinder is closed at the lower end, or that it is carried liquid-tight on, or through, the supporting solid surface underneath. On either alternative, the conditions in the immediate neighbourhood of  $z=0$  are determined partly by the flat base or the supporting flat solid; and if the cylinder be short compared to its diameter, more especially if its walls be thick, the solution we have obtained above will not be satisfactory. If, however, the walls be thin, as in an ordinary glass beaker, the solution will, I think, prove in general sufficiently accurate.

As illustrating the nature of the solution, suppose the outer cylindrical surface free of stress, whilst inside there is liquid of density  $\rho'$  to a height  $h$ . Then, if  $\Pi_0$  be the atmospheric pressure at the surface of the liquid, the pressure at a height  $z$  above the base of the cylinder is  $\Pi_0 + g\rho'(h-z)$ . As this equals by hypothesis  $\Pi' + C'z$ , we have

$$\Pi = \Pi_0 + g\rho h, \quad C' = -g\rho'.$$

The law of pressure holds only between the values 0 and  $h$  of  $z$ , and the solution must be similarly restricted. In such

a case we should take

$$l=h,$$

$\pi(a^2 - a'^2)Z = \text{weight of tube above level of liquid.}$

§ 13. The internal and external pressure systems in (40) and (41) are quite independent, but for brevity we shall regard them as coexistent and applicable up to the same height  $h$  above the base. Let  $p$  and  $p'$  be the external and internal pressures at the height  $h/2$  above the base, and  $H + h/2$  the total height of the cylinder, so that

$$\left. \begin{aligned} \Pi + \frac{1}{2}Ch &= p, \\ \Pi' + \frac{1}{2}C'h &= p', \\ Z + \frac{1}{2}g\rho h &= g\rho H \end{aligned} \right\} \dots \dots \dots (42)$$

The volumes enclosed by the outer and inner surfaces up to a height  $h$  in the original unstrained state are

$$v_o = \pi a^2 h, \quad v_i = \pi a'^2 h.$$

The elastic increment in the volume within the outer surface is given by

$$\delta v_o = 2\pi a \int_0^h u_{r=a} dz + \pi a^2 \{w_{z=h} - w_{z=0}\}_{r=a}$$

and the corresponding increment  $\delta v_i$  of the volume within the inner surface is given by an analogous formula. After some reduction we obtain from (41) and (42), noticing that  $l \equiv h$ ,

$$\left. \begin{aligned} \delta v_o/v_o &= -\frac{g\rho H}{3k} - \frac{a'^2}{a^2 - a'^2} \frac{p - p'}{n} - \frac{2}{3k} \frac{pa^2 - p'a'^2}{a^2 - a'^2}, \\ \delta v_i/v_i &= -\frac{g\rho H}{3k} - \frac{a^2}{a^2 - a'^2} \frac{p' - p}{n} - \frac{2}{3k} \frac{p'a'^2 - pa^2}{a^2 - a'^2}, \\ \frac{\delta(v_o - v_i)}{v_o - v_i} &\equiv \frac{\delta v}{v} = -\frac{1}{3k} \left\{ g\rho H + 2 \frac{pa^2 - p'a'^2}{a^2 - a'^2} \right\}. \end{aligned} \right\} \dots (43)$$

The elastic changes in the volumes  $v_o$  and  $v_i$ , as well as in the volume  $v (= v_o - v_i)$  of the cylindrical walls, are exactly the same as if the pressure over each surface had a constant value equal to its mean value.

The term  $g\rho H/(3k)$  depends only on the weight and elastic properties of the tube itself, and so may be left out of account

in considering the influence of the liquid pressures. Omitting it, we see that if a circular tube be filled with liquid of density  $\rho'$  to a mark at height  $h$ , the volume within the tube up to the mark is increased to an extent  $\delta v_i$  which is given by

$$\begin{aligned}\delta v_i/v_i &= \frac{1}{2} g \rho' h \{ (a^2/n) + 2(a^3/3k) \} / (a^2 - a'^2) \\ &= g \rho' h \{ (1 + \eta) a^2 + (1 - 2\eta) a'^2 \} / \{ E(a^2 - a'^2) \} . \quad (44)\end{aligned}$$

If the thickness  $t$  of the walls of the tube be small compared to  $a$ , this becomes approximately

$$\delta v_i/v_i = \frac{1}{2} g \rho' h (a/t) (2 - \eta) / E . \quad (45)$$

The increase in volume per unit of volume inside a thin-walled tube thus varies directly as the density of the liquid, the height of the mark, and the radius of the tube, while it varies inversely as the thickness of the wall. We see that for exact purposes the cubic capacity of a tube cannot be defined without reference to the density of the liquid which it is to contain; also all copies of a standard of capacity should be identical in height, diameter, thickness, and elasticity.

As a numerical illustration, suppose a tube of glass 1 cm. radius, with walls 1 mm. thick, to hold (i.) water, (ii.) mercury, to a height of 16 cm. This gives a content of about 50 c.c., and the increments in the capacity in the two cases are approximately, if we assume  $\eta = 1/4$  and  $E = 6 \times 10^8$  grammes weight per sq. cm.,

$$(i.) \delta v_i = 12 \times 10^{-6} \text{ c.c.},$$

$$(ii.) \delta v_i = 16 \times 10^{-5} \text{ c.c.}$$

In case (ii.) the tube holds fully 2 milligrams more of mercury than if it were absolutely non-elastic.

As a second example, take the case of a glass tube whose height is 12.7 cm., internal diameter 10 cm., thickness 1.5 mm., for which  $E$  and  $\eta$  have the values assumed above. The internal capacity is approximately 1000 c. c.; and the elastic increments when the tube is full of (i.) water, (ii.) mercury, are approximately

$$(i.) \delta v_i = 62 \times 10^{-5} \text{ c.c.},$$

$$(ii.) \delta v_i = 84 \times 10^{-4} \text{ c.c.}$$



This tube thus holds about 0.11 gramme more mercury than if it were wholly inelastic.

*Spherical Shell containing and surrounded by Liquid.*

§ 14. Another instance in which we can find the changes of the volumes enclosed by the outer and inner surfaces of a hollow vessel, containing and surrounded by liquid, is that of a spherical shell; but only when it is in equilibrium under its own weight and the pressure systems. Thus external pressure is necessarily existent, though internal pressure is not.

Take the origin at the common centre, the outer and inner surfaces being respectively of radii  $a$  and  $a'$ . Draw the axis of  $z$  vertically downwards, and suppose the pressure to be  $p + g\rho'z$  outside and  $p' + g\rho''z$  inside, so that  $\rho'$ ,  $\rho''$  represent the densities of the liquids. In order that equilibrium may exist, the density  $\rho$  of the shell must be connected with the densities of the liquids by the relation

$$\rho(a^3 - a'^3) = \rho'a^3 - \rho''a'^3. \quad (46)$$

There is obviously symmetry round the vertical diameter, and the displacements  $u$  along, and  $w$  perpendicular to, the radius vector  $r$  depend only on  $r$  and the inclination  $\theta$  of  $r$  to the axis of  $z$ . The values of the displacements are

$$u = -\frac{r(pa^3 - p'a'^3)}{(3m-n)(a^3 - a'^3)} - \frac{(aa')^3 r^{-2}(p-p')}{4n(a^3 - a'^3)} \\ + \frac{gr^2 \cos \theta}{6(m+n)(3m-n)} \left\{ 2(m-2n) \frac{\rho'a^5 - \rho''a'^5}{a^5 - a'^5} - (5m-n) \frac{\rho'a^3 - \rho''a'^3}{a^3 - a'^3} \right\} \\ - \frac{gr^{-1} \cos \theta (\rho' - \rho'')(aa')^3}{3n(a^3 - a'^3)} - \frac{gr^{-3} \cos \theta (\rho' - \rho'')(aa')^5}{9(m+n)(a^5 - a'^5)}, \quad (47)$$

$$w = \frac{gr^2 \sin \theta}{6(m+n)(3m-n)} \left\{ (m-n) \frac{\rho'a^3 - \rho''a'^3}{a^3 - a'^3} - 2(2m+n) \frac{\rho'a^5 - \rho''a'^5}{a^5 - a'^5} \right\} \\ + \frac{gr^{-1} \sin \theta (m+2n)(\rho' - \rho'')(aa')^3}{6n(m+n)(a^3 - a'^3)} - \frac{gr^{-3} \sin \theta (\rho' - \rho'')(aa')^5}{18(m+n)(a^5 - a'^5)}. \quad (48)$$

As  $r \cos \theta \equiv z$ , all terms in  $u$  which depend on  $\theta$  change sign as we cross the horizontal plane through the centre.

The change in the volume  $v_r (\equiv 4\pi r^3/3)$  enclosed by any spherical surface concentric with the shell ( $a > r > a'$ ) is

given by

$$\delta v_r = \int_0^\pi 2\pi u r^2 \sin \theta d\theta.$$

As the integral of  $\sin \theta \cos \theta$  between 0 and  $\pi$  vanishes, the only terms in  $u$  which contribute to  $\delta v_r$  are those containing  $p$  or  $p'$ ; and it will be found that the increments in the volumes within the outer and inner surfaces and in that of the material are respectively given by

$$\left. \begin{aligned} \delta v_o/v_o &= -\{(pa^3 - p'a'^3)/(k) + 3(p - p')a'^3/(4n)\} + (a^3 - a'^3), \\ \delta v_i/v_i &= -\{(pa^3 - p'a'^3)/(k) + 3(p - p')a^3/(4n)\} \div (a^3 - a'^3), \\ \delta v/v &= -\{pa^3 - p'a'^3\} \div \{k(a^3 - a'^3)\}, \end{aligned} \right\} \quad (49)$$

$$\text{or } \delta v = -4\pi(pa^3 - p'a'^3)/3k.$$

These changes are the same as if the outer and inner surfaces were exposed to uniform pressures  $p$  and  $p'$ . They do not depend directly on  $\rho$ ,  $\rho'$ , or  $\rho''$ , and at first sight one might be tempted to assume that the expressions were perfectly general. This, however, is not the case. If, for instance, the vessel were wholly or partially supported on a horizontal plane, we should obtain from the general formula (2) for the change in the volume  $v$  of the material of the shell

$$\delta v = -4\pi(pa^3 - p'a'^3)/(3k) - Za/3k; \quad . \quad . \quad (50)$$

where

$$Z \equiv (4/3)\pi g\{\rho(a^3 - a'^3) - (\rho'a^3 - \rho''a'^3)\} \quad . \quad (51)$$

is the total upward thrust exerted by the supporting plane.

This expression for  $\delta v$  accords with the previous one only when  $Z$  vanishes, *i. e.* when no part of the weight is borne by the plane.

Another limitation to the generality of the results (49) is that the pressures  $p + g\rho'z$  and  $p' + g\rho''z$  are assumed to hold over the whole of their respective surfaces. Thus the shell must be wholly immersed, and it must be either quite full or quite empty of liquid.

The results would doubtless be very approximately true for a wholly immersed flask consisting of a spherical body and narrow cylindrical neck, the contained liquid, if any, extending into the neck. If necessary an allowance might be made, from the data in § 12, for the change in volume of the neck.

*Cylinder under Pressure a Quadratic Function of  $z$ .*

§ 15. The method of § 6 would enable us to calculate the change in the total volume of a solid vertical cylinder of any form of section when exposed to a pressure which is a quadratic function of the vertical coordinate  $z$ . When the section is circular we can obtain, however, what is in most cases a satisfactory *complete* solution for this law of pressure. As we have already dealt with the case when the pressure is a linear function of  $z$ , we need consider in addition only the elastic displacements, strains, and stresses due to a pressure varying as  $z^2$ . Employing  $r, z$  as in § 12, and making use of my solution \* in ascending powers of  $r$  and  $z$ , I find for the axial and longitudinal displacements due to a pressure  $q'z^2$  on the cylindrical surface  $r=a$ ,

$$\left. \begin{aligned} u &= (q'/E) \left\{ \frac{1}{4}\eta r(a^2 - r^2) - (1-\eta)rz^2 \right\}, \\ w &= (q'/E) \left\{ \frac{1}{2}(1-\eta)z(2r^2 - a^2) + \frac{2}{3}\eta z^3 \right\} \end{aligned} \right\} . \quad (52)$$

The corresponding stresses are

$$\left. \begin{aligned} \widehat{rr} &= \widehat{\phi\phi} - \frac{1}{2} \frac{\eta}{1+\eta} q' r^2 = -\frac{1}{2} \frac{\eta}{1+\eta} q' (a^2 - r^2) - q' z^2; \\ \widehat{zz} &= \frac{1}{2} \frac{q'}{1+\eta} (2r^2 - a^2); \\ \widehat{r\phi} &= \widehat{rz} = \widehat{\phi z} = 0. \end{aligned} \right\} . \quad (53)$$

This solution is not altogether complete, supposing no forces to act except on the curved surface; for, instead of making  $\widehat{zz}$  vanish at every point of the flat ends, it only gives

$$\int_0^a 2\pi r z \widehat{rr} dr = 0.$$

According, however, to St. Venant's theory of equipollent systems of loading, this defect is very trifling in a long cylinder except in the immediate neighbourhood of the ends.

As an example, suppose the pressure arises from a liquid whose density follows the law  $\rho'(1-2qz)$ , where  $z$  is measured upwards from the base of the cylinder. This includes the case of a compressible liquid treated in § 5. The pressure  $p$  in the liquid follows the law

$$p = \Pi - g\rho'(1-qz), \quad . \quad . \quad . \quad . \quad (54)$$

\* Camb. Phil. Trans. vol. xiv. l. c.

where  $\Pi$  is the pressure at the level of the base of the cylinder; thus in applying the solution just obtained we replace  $q'$  by  $g\rho'q$ . The complete values of the displacements and stresses are as follows, the notation being as before, and the cylinder being supposed suspended:—

$$\left. \begin{aligned} u &= -E^{-1}r[(1-2\eta)\Pi + gz\{\eta\rho - (1-\eta)\rho'\}] \\ &\quad + E^{-1}g\rho'qr\{\frac{1}{4}\eta(a^2 - r^2) - (1-\eta)z^2\}, \\ w &= -E^{-1}z[(1-2\eta)\Pi - \frac{1}{2}gz(\rho - 2\eta\rho')] + \frac{1}{2}E^{-1}gr^2\{\eta\rho - (1-\eta)\rho'\} \\ &\quad + E^{-1}g\rho'qz\{\frac{1}{2}(1-\eta)(2r^2 - a^2) + \frac{2}{3}\eta z^2\}; \end{aligned} \right\} \quad (55)$$

$$\left. \begin{aligned} \widehat{rr} &= \widehat{\phi\phi} - \frac{1}{2} \frac{\eta}{1+\eta} g\rho'qr^2 = -\Pi + g\rho'z(1-qz) \\ &\quad + \frac{1}{4} \frac{\eta}{1+\eta} g\rho'q(a^2 - r^2) - g\rho'qz^2, \\ \widehat{zz} &= -\Pi + g\rho z + \frac{1}{2} \frac{g\rho'q}{1+\eta} (2r^2 - a^2), \\ \widehat{r\phi} &= \widehat{rz} = \widehat{\phi z} = 0. \end{aligned} \right\} \quad (56)$$

Over the base  $z=0$  the mean value of  $-\widehat{zz}$  is  $\Pi$ , that being by hypothesis the pressure at this depth in the liquid.

If  $h$  be the height of the cylinder, the suspending forces are given by

$$\widehat{zz} = -\Pi + g\rho h + \frac{1}{2}g\rho'q(2r^2 - a^2)/(1+\eta),$$

the mean value over the cross section being  $-\Pi + g\rho h$ . This is a pull or a push according as  $g\rho h$  or  $\Pi$  is the larger.

The elastic change in the radius at height  $z$  is given by

$$\delta a/a = -\{(1-2\eta)\Pi + g\rho\eta z - g\rho'(1-\eta)z(1-qz)\}/E. \quad (57)$$

The mean change in height (*i. e.* the mean difference between the values of  $w$  over the cross sections  $z=h$  and  $z=0$ ) is given by

$$\delta \bar{h}/h = \{2\eta\bar{p} - (\Pi - \frac{1}{2}g\rho h)\}/E, \quad \dots \quad (58)$$

where

$$\bar{p} \equiv \Pi - \frac{1}{2}g\rho'h(1 - \frac{2}{3}qh). \quad \dots \quad (59)$$

is the mean value of the liquid pressure throughout the height of the cylinder.

The modification required to adapt the preceding solution to the case when the cylinder is supported on its base is easily applied.

*General Properties ; Influence of Cavities ; Gravitation, &c.*

§ 16. Some general conclusions may be derived from (2) as to the influence of cavities in solids exposed only to surface forces. If we distinguish the external surface and the several internal surfaces limiting cavities, with their respective force systems, by suffixes, (2) becomes in the absence of bodily forces

$$3k\delta v = \iint (F_1x + G_1y + H_1z) dS_1 + \iint (F_2x + G_2y + H_2z) dS_2 + \dots \quad (60)$$

As each of the surface integrals is self-contained, we see that if a given system of forces act over a given surface, the total change produced in the volume of the material is independent of the existence of cavities. For instance, if given forces act over an outer spherical surface, the change in the *total* volume of the material within it is the same whether the sphere be absolutely solid, or whether it contain a cavity or cavities over whose surfaces no forces act. If there is a large cavity, the mean change of volume *per unit volume* is correspondingly greater.

If a uniform pressure  $p_1$  act over a surface  $S_1$ , the corresponding change of volume is given by

$$3k\delta v = -p_1 \iint (\lambda_1 x + \mu_1 y + \nu_1 z) dS_1 = -3p_1 v_1,$$

or

$$\delta v = -p_1 v_1 / k, \quad \dots \dots \dots (61)$$

where  $v_1$  is the volume of the space enclosed by  $S_1$ .

If, then, uniform pressure of given intensity be applied over the surface of a cavity, the total change of volume in the material depends only on the *volume* of the cavity, and is independent of its form or position, or of the extent of the solid, supposing it bounded by free surfaces.

§ 17. There are also some simple general properties deducible from (2) in the case of isotropic material acted on only by bodily forces following the gravitational law.

Thus, suppose a centre of gravitational force at the origin of coordinates, and so

$$X/x = Y/y = Z/z = -m/r^3, \quad \dots \dots (62)$$

where  $m$  is a constant. The corresponding elastic increment

in the volume of the solid is by (2)

$$\delta v = -(m/3k) \left[ \iiint r^{-1} dx dy dz \right], \quad . \quad . \quad (63)$$

the integral extending throughout the whole solid.

But the integral, within the square brackets, simply represents the potential at the origin answering to a distribution of unit density throughout  $v$ . Thus the change in volume of the solid varies as the value of its potential at the centre of force, and can be calculated when the potential can. If, for instance, the solid were a sphere whose centre was at a distance  $R$  from the centre of force, we should have

$$\delta v/v = -m/(3kR). \quad . \quad . \quad . \quad (64)$$

It is clear from (63) that the change of volume is unaltered by moving the centre of force from any one point to any other point which lies on the same equipotential surface of the solid.

In applying (63) it must be borne in mind that in general a body cannot be in equilibrium under the action of a single centre of force, and that when equilibrium exists under the joint action of a number of centres of force it is to a certain extent arbitrary to regard the effect of one as independent of the others. In the case of a planet, for instance, the "centrifugal force" in the orbital path balances the sun's attraction. If we regarded the planet as an elastic solid describing a circular path, and neglected for the time being the effects of self-gravitation and rotation about an axis, we should find its elastic change of volume given by two terms. One of these terms would be of the type (64), depending on the mass of the sun; the other would depend on the angular velocity in the orbit. The persistence, however, of the planet in its orbit implies a necessary relation between the gravitational and "centrifugal" forces, so that the two terms in the expression for  $\delta v$  could be combined into one, containing as we choose the angular velocity or the gravitational constant.

§ 18. In obtaining (63) we treated the source of the gravitational forces as wholly external to the solid. In a self-gravitating homogeneous spherical "earth" of radius  $a$ , we should have.

$$X/x = Y/y = Z/z = -g\rho/a,$$

where  $g'$  is "gravity" at the surface. Substituting in (2) we easily deduce

$$\delta v/v = -g'\rho a/5k. \quad . \quad . \quad . \quad . \quad (65)$$

As I have repeatedly remarked elsewhere, the application of such a formula to the actual earth—or other principal planet—leads to numerical results which cannot be reconciled with the fundamental hypotheses of mathematical elasticity unless  $k$  be much larger than in known materials under the conditions existing near the earth's surface.

In small bodies, on the other hand, the effects of self-gravitation are very small. For instance, for a sphere of iron ( $\rho=7.5$ ,  $k=15 \times 10^8$  grammes wt. per sq. cm.) of one metre radius we should get from (65)

$$\delta v/v = -2 \times 10^{-14},$$

or

$$\delta a = -7 \times 10^{-12} \text{ mm.}$$

### *Standards of Length.*

§ 19. If a rectangular prism of horizontal length  $L$  be placed on a perfectly smooth and horizontal plane, we find from (36) for the elastic increment in the length at a height  $\frac{h}{2} + z$  above the plane ( $h$  being the vertical dimension of the prism) the formula

$$\delta L/L = -(1-2\eta)(p/E) + \eta g(\rho - \rho') (h/2E) - gz\{\eta\rho - (1-\eta)\rho'\}/E. \quad (66)$$

Here  $p$  represents, as before, the pressure in the liquid or gaseous medium surrounding the prism at the level of the C.G., *i. e.* at the height  $h/2$  above the plane. This result should apply to an ordinary standard yard, and to most commercial standards of length, if supported throughout the entire length on a perfectly smooth table. If, as in the standard yard, the scale is divided on the upper surface  $z=h/2$ , we have for its elastic stretching

$$\begin{aligned} \delta L/L &= -\frac{(1-2\eta)}{E} \left( p - g\rho' \frac{h}{2} \right) \\ &= -P/3k, \quad . \quad . \quad . \quad . \quad . \quad (67)* \end{aligned}$$

\* [Oct. 1901.—A formula apparently equivalent to this is given without proof by Mr. Chaney, on pp. 86, 87 of the *Procès Verbaux* of the International Committee of Weights and Measures for 1899. It is given as applicable to the standard yard, without explicit reference to the method of support, and is illustrated numerically.]

where  $P$  is the pressure in the medium at the level of the divided surface, and  $k$  is the bulk-modulus.

When the prism is not of rectangular section, or when, being of rectangular section, it is supported on points or roller surfaces situated in a horizontal plane, we have to content ourselves with the *mean* change in the length of the longitudinal "fibres." For this we find from (1),  $H$  being the height of the C.G. of the section above the supports,

$$\delta L/L = -(1 - 2\eta)(p/E) + \eta g(\rho - \rho')(H/E), \quad (68)$$

where  $p$  is the pressure in the surrounding medium at the height  $H$ .

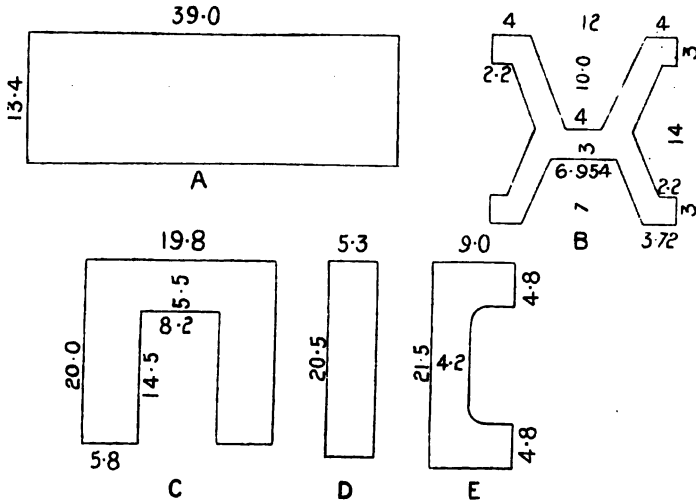
In the case of the rectangular section, with the base uniformly supported, it follows from (66) that the mean change in the length is the change actually occurring at the level of the C.G. ; but we are not entitled to assume that this is true generally. This is a question of some theoretical importance in view of the now common practice of dividing standards of length along the so-called "neutral" surface, *i. e.* the horizontal plane containing the C.G.

§ 20. To afford a more exact idea of the problems actually arising in metrology, I give in fig. 1 some representative forms of cross section in standards of length. The sides shown vertical in the figure are vertical in ordinary use ; the numerals refer to the dimensions, and are in millimetres. A refers to a standard yard, B to the international prototype metres of the so-called X-section, C to a working standard belonging to the Bureau International, D and E to deflexion-bars used in magnetometers. A and C are divided on their upper surfaces, B on the neutral plane, D on one of the vertical faces ; E has holes on its upper surface into which a plug fits. B and C are copied from vol. vii. of the Bureau International's *Travaux et Mémoires*. Their shape is devised partly with the object of facilitating equalization of temperature throughout the bar. Most modern standards are supported not over the whole lower surface but on two symmetrical rollers, or on three points, one at one end of the bar, and two—in the same cross section—at the other end. This mode of support is intended to promote uniformity of temperature, the bar being surrounded by liquid, and to



remove the uncertainty as to the distribution of surface-pressure when a bar rests on an ordinary table, and not on an ideal smooth plane \*.

Fig. 1.

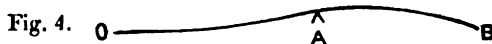
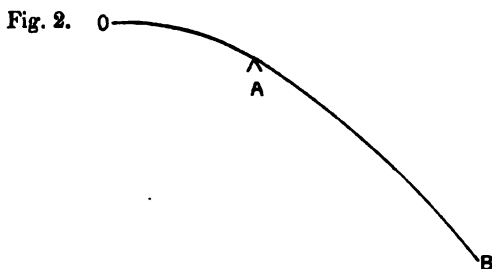


An exact solution of the elastic problem presented by a heavy bar supported on points or rollers has not yet been obtained even for a rectangular section, and the best thing to be done is probably to apply the ordinary approximate Bernoulli-Euler solution. From the researches of St. Venant, Pearson, and others we have grounds to believe that for bars like standard yards and metres, whose length is a large multiple of their greatest lateral dimension, the Bernoulli-Euler solution represents a high degree of accuracy except perhaps in the immediate vicinity of the supports. Actual observations on standards of the types B and C by Broch and Benoit (*Trav. et Mém.* l. c.) seem to bear this out. The Bernoulli-Euler method of solution is so well known that it is unnecessary to describe it, and the results which I am now about to give are deducible from the solution without much difficulty. Some of them have, I find, been given by Airy and by Broch, *l. c.*, and possibly this remark applies to more than I am aware of; but I do not think they are generally known.

\* See Airy (*Phil. Trans.* for 1857).

*Applications of Bernoulli-Euler Method.*

§ 21. In figs. 2 to 6, OB represents the *half* of a bar of uniform section  $\omega$  and total length  $2l$  supported symmetrically at two points in a horizontal plane at a distance  $2a$  apart. From the symmetry the tangent at the middle point O is horizontal; this is taken as axis of  $x$ , the axis of  $y$  being drawn vertically downwards. In fig. 2 the support shown, A, is comparatively near the centre. In such a case O is the



highest point of the bar bent under its own weight, and the curvature is of one sign throughout. In figs. 3 to 6 the supports are at a greater distance from the centre, and the curvature changes sign between O and A; this is the normal condition in modern standards of length. The scale to which the ordinates are drawn is the same in all the figures 2 to 6, the bending being much exaggerated.

The notation employed is as follows:—E is Young's

modulus,  $\rho$  the density,  $2l$  the complete length of the bar,  $\omega$  the cross section,  $w (= g\rho\omega)$  the weight per unit length,  $\omega\kappa^2$  the moment of inertia of the cross section about the perpendicular through the C.G. to the plane of bending.

In the absence of gravity the bar would be strictly horizontal;  $y$  denotes the vertical displacement, when gravity acts, at the distance  $x$  from 0 along the "neutral" line, or line of centres of the cross sections. What principally concerns us at present is the inclination or "slope" and the curvature, so I give the values of  $dy/dx$  and  $d^2y/dx^2$  as well as  $y$ ; the results of course are well known. They are as follows,  $y$  being taken positive downwards.

Between 0 and A :—

$$\left. \begin{aligned} y &= (w/E\omega\kappa^2) \left\{ \frac{1}{2}l(\frac{1}{2}l-a)x^2 + \frac{1}{24}x^4 \right\}, \\ dy/dx &= (w/E\omega\kappa^2) \left\{ l(\frac{1}{2}l-a)x + \frac{1}{6}x^3 \right\}, \\ d^2y/dx^2 &= (w/E\omega\kappa^2) \left\{ l(\frac{1}{2}l-a) + \frac{1}{2}x^2 \right\}. \end{aligned} \right\} \quad \dots \quad (69)$$

Between A and B :—

$$\left. \begin{aligned} y &= (w/E\omega\kappa^2) \frac{1}{24} \{ 4la^3 - l^4 + 4lx(l^2 - 3a^2) + (l-x)^4 \}, \\ dy/dx &= (w/E\omega\kappa^2) \frac{1}{6} \{ l(l^2 - 3a^2) - (l-x)^3 \}, \\ d^2y/dx^2 &= (w/E\omega\kappa^2) \frac{1}{2} (l-x)^2. \end{aligned} \right\} \quad (70)$$

§ 22. On the Bernoulli-Euler theory the elastic extension in an element  $ds$  of a longitudinal "fibre" at a distance  $h$  above the neutral plane is  $(h/R)ds$ , where  $R$  is the radius of curvature of the bent neutral line. But if  $\psi \equiv \tan^{-1}(dy/dx)$ , we have

$$1/R = d\psi/ds,$$

and so

$$(h/R)ds = h d\psi.$$

Thus the total stretching  $\sigma_x$  in the portion of a longitudinal fibre—distant  $h$  from the neutral plane—extending from the central section  $x=0$  to the section where the slope is  $\psi$ , is given by

$$\begin{aligned} \sigma_x &= \int_0^\psi h d\psi = h\psi \\ &= h dy/dx, \dots \dots \dots (71) \end{aligned}$$

when  $(dy/dx)^2$  is neglected compared to unity.

In fig. 2,  $dy/dx$  and  $d^2y/dx^2$  are positive for all values of  $x$  from 0 to  $l$ ; thus a longitudinal fibre is stretched at every.

point of its length, or contracted at every point of its length, according as  $h$  is positive or negative, *i. e.* according as the fibre lies above or below the neutral plane.

In fig. 3, a longitudinal fibre above the neutral plane would shorten in its central portion, while lengthening near its ends.

The ordinary expression for the curvature, viz.:

$$1/R = (d^2y/dx^2)(1 + (dy/dx)^2)^{-\frac{3}{2}},$$

is on the Bernoulli-Euler theory replaced by

$$1/R = d^2y/dx^2;$$

so that  $(dy/dx)^2$  is neglected as compared to unity whenever the use of this theory is warranted.

On the theory, the length of the neutral fibres (for which  $h=0$ ) measured *along the arc* is unaffected by stretching. In standards of length, however, it is the horizontal projection of the graduated surface that usually concerns us. We thus require to know how much shorter  $x$  is than  $s$ , the latter denoting the length of a neutral fibre measured from the centre of the bar along the arc.

We have in any plane curve

$$s - x = \int_0^x \{ (1 + (dy/dx)^2)^{\frac{1}{2}} - 1 \} dx. \quad \dots \quad (72)$$

As  $(dy/dx)^2$  is supposed neglected compared to unity, we can consistently retain only the lowest power of  $dy/dx$  in such a formula as (72), and so get

$$s - x = \int_0^x \frac{1}{2} (dy/dx)^2 dx \quad \dots \quad (72')$$

For instance, we have from (69) and (70) for the difference between arc and chord for the entire length of the bar,

$$\begin{aligned} 2(s_l - l) &= \int_0^a (w/E\omega\kappa^2)^2 \left\{ l(-a + \frac{1}{2}l).x + \frac{1}{6}x^3 \right\}^2 dx \\ &\quad + \int_a^l (w/E\omega\kappa^2)^2 \left\{ -\frac{1}{2}lx^2 + \frac{1}{6}l^3 - \frac{1}{6}(l-x)^3 \right\}^2 dx \\ &= l(wl^3/E\omega\kappa^2)^2 \left\{ \frac{1}{56} - \frac{1}{8}\left(\frac{a}{l}\right)^2 + \frac{7}{24}\left(\frac{a}{l}\right)^4 - \frac{2}{15}\left(\frac{a}{l}\right)^6 + \frac{1}{360}\left(\frac{a}{l}\right)^8 \right\} \quad (73) \end{aligned}$$

An equivalent formula is given by Broch (*l. c.* formula (16) p. B. 67). The right-hand side represents the quantity by

which the distance between the extreme ends of the bar is shortened through the bending which it experiences under gravity, when supported symmetrically at two points at a distance  $2a$  apart.

It will be observed that  $\sigma_x$  is of the order  $hdy/dx$ , or  $h(wl^3/E\omega\kappa^2)$ , and  $s-x$  is of the order  $x(wl^3/E\omega\kappa^2)^{1/2}$ ; while by the hypothesis made as to the smallness of  $dy/dx$  we must suppose  $wl^3/E\omega\kappa^2$  a small quantity. Thus unless  $x/h$  be very big, *i. e.* unless we have a very long bar, or are considering fibres very close to the neutral plane, the difference between chord and arc is small compared to the direct stretching or shortening of the fibre.

§ 23. Owing to the symmetry, we need consider only the half of the bar for which  $x$  is positive. In all cases  $dy/dx$  vanishes at the centre. It also vanishes at a point (real or imaginary) between the centre and support whose abscissa is given by

$$x_2 = l \{ 3(2a/l - 1) \}^{1/2} \quad (74)$$

To apply to our problem,  $x_2$  must be real and less than  $a$ ; this is true only when  $a/l$  lies between 0.5 and  $3 - \sqrt{6}$ , or .5505.

Between the support and the end,  $dy/dx$  vanishes for a point whose abscissa is given by

$$x_3 = l - l(1 - 3a^2/l^2)^{1/2} \quad (75)$$

This applies to our problem only when  $a/l$  lies between  $3 - \sqrt{6}$  (or .5505) and  $\sqrt{1/3}$  (or 0.57735).

In all cases  $d^2y/dx^2$  vanishes at the end of the bar. It vanishes at the centre when  $a/l = 1/2$ . Between the centre and the support it vanishes at a point whose abscissa is given by

$$x_1 = l(2a/l - 1)^{1/2} \quad (76)$$

and at this point we find

$$(dy/dx)_{x_1} = - (wl^3/E\omega\kappa^2)^{1/2} (x_1/l)^3 = - (wl^3/E\omega\kappa^2)^{1/2} (2a/l - 1)^{3/2} \quad (77)$$

These values of  $x$  and  $dy/dx$  are real, and apply to our problem whenever  $a/l$  exceeds 1/2. When  $a/l > 1/2$ , we have  $dy/dx$  negative and  $d^2y/dx^2$  positive at  $x = x_1$ ; and it follows that  $dy/dx$ , numerically considered, is here a maximum. When  $a/l$  is less than 1/2,  $dy/dx$  is positive between the centre and

the support, and its value at the support is greater than at any point nearer the centre. At the support we have

$$(dy/dx)_s = (wl^3/E\omega\kappa^2)^{\frac{1}{8}}(a/l)\{(a/l)^3 - 6(a/l) + 3\}. \quad (78)$$

This is positive or negative according as  $a/l$  is less or greater than 0.5505. Beyond the support  $d^2y/dx^2$  can vanish only at the end, where we have

$$(dy/dx)_l = (wl^3/E\omega\kappa^2)^{\frac{1}{8}}\{1 - 3(a/l)^2\}. \quad (79)$$

This is positive or negative according as  $a/l$  is less or greater than  $1/\sqrt{3}$ . When  $dy/dx$  is positive for a certain value of  $x$ , the total length of a longitudinal fibre between the central section  $x=0$  and the section considered is increased when the fibre lies above the neutral plane; and the element of the fibre answering to this value of  $x$  has also its length increased if  $d^2y/dx^2$  be positive. If, on the other hand, while  $dy/dx$  is positive,  $d^2y/dx^2$  is negative, the *element* is shortened though the total length is still increased. Answering to  $d^2y/dx^2=0$ , we get, included between the corresponding value of  $x$  and the centre, that particular length whose total extension is a maximum. If  $dy/dx$  vanishes for two values of  $x$ , then the portion of any longitudinal fibre included between the two corresponding transverse sections has its total length unchanged by stretching. These remarks will, it is hoped, suffice to explain how the conclusions in the next paragraph are reached.

§ 24. The bending of a symmetrically supported bar under its own weight may be conveniently dealt with under several cases as follows :—

*Case (i.)* Fig. 2,  $a/l < 0.5$ .

The upper surface is everywhere convex (stretched). The slope vanishes only at the centre, and is greatest at the end.

*Case (ii.)* Fig. 3,  $0.5505 > a/l > 0.5$ .

The upper surface is concave (contracted) between  $x=x_0$  and  $x=x_1$  (where  $x_1 < a$ ), and convex (stretched) between  $x=x_1$  and the end. The “summit,” where the slope vanishes, occurs at  $x=x_2$  (where  $x_2 = 3^{\frac{1}{2}}.r_1$ ) between the centre and the support.

Between the centre and the summit the steepest slope occurs at  $x=x_1$ ; beyond the summit the slope is steepest at the end, and the slope at the end is greater than at  $x=x_1$ .

*Case (iii.)* Fig. 4,  $0.5654 > a/l > 0.5505$ .

This agrees with Case (ii.) except in the following respects:—

The summit occurs at  $x=x_2$  between the support and the end.

The slope is greater at  $x=x_1$  than at the end when  $a/l > 0.5$ .

*Case (iv.)* Fig. 5,  $0.57735 > a/l > 0.5654$ .

The upper surface is concave (contracted) between  $x=0$  and  $x=x_1$  (where  $x_1 < a$ ), and convex (stretched) between  $x=x_1$  and the end.

The summit occurs at  $x=x_2$  between the support and the end.

The slope is greatest at  $x=x_1$  between the centre and the support, and is greater at the support than at the end or at any intermediate point.

*Case (v.)* Fig. 6,  $a/l > 0.57735$ .

This agrees with Case (iv.) except that the slope vanishes only at the centre.

What is said above of the "upper surface" applies to all longitudinal "fibres" above the neutral plane. For absolute accuracy the decimals 0.5505, 0.5654, and 0.57735 are to be respectively replaced by  $3-\sqrt{6}$ , the positive root of  $z^3-9z^2+3z+1=0$ , and  $\sqrt{1/3}$ .

§ 25. Every element of the upper surface is stretched in Case (i.). Thus it is impossible to keep the length of any finite portion of the upper surface unaffected unless  $a/l$  exceed 0.5. By altering  $a/l$  we can secure that any symmetrical portion we choose of the upper surface shall have its length unaffected. We have only to make the slope *nil* at the ends of the portion considered.

Denoting the symmetrical length to be kept unaffected by  $2b$ , we have the position of the supports given by one or other of two equations, viz.:—

$$a/l = \frac{1}{2} + \frac{1}{6}(b/l)^2, \quad . \quad . \quad . \quad . \quad . \quad (80)$$

when  $b/l$  lies between 0 and  $\cdot 5505$ ;

$$a/l = \left[ \frac{1}{3} \{ 1 - (1 - b/l)^3 \} \right]^{\frac{1}{2}}, \quad \dots \quad (81)$$

when  $b/l$  exceeds  $\cdot 5505$ .

Any given arrangement of the supports secures the unchangeability of only one definite symmetrical portion of the length. We may, however, have unchangeability of length in an asymmetrical portion. Supposing the unchanged length wholly included between the centre and a support, its terminal abscissæ being  $\xi_1$  and  $\xi_2$ , we find by equating the terminal values of  $dy/dx$ ,

$$\begin{aligned} \xi_1^2 + \xi_1 \xi_2 + \xi_2^2 &= 3(2al - l^2) \quad \dots \quad (82) \\ &= 3x_1^2, \text{ or } x_2^2 \text{ by (76) and (74).} \end{aligned}$$

Regarding  $\xi_1$  and  $\xi_2$ , and so  $x_1$ , as known, we determine the position of the supports from the equation

$$a/l = \frac{1}{3} + \frac{1}{6}(\xi_1^2 + \xi_1 \xi_2 + \xi_2^2)/l^2 = \frac{1}{3} \{ 1 + (x_1/l)^2 \}. \quad \dots \quad (83)$$

This applies only when  $a/l$  exceeds  $0\cdot 5$ .

Answering to any given value of  $a/l$  exceeding  $0\cdot 5$ , we have an infinite number of pairs of values  $\xi_1, \xi_2$ . The ends of the asymmetrical portion necessarily lie on opposite sides of the point  $x = x_1$  where the slope is a maximum.

In cases (iii.), (iv.), and (v.) we can have unchanged length in an asymmetrical portion whose ends lie on opposite sides of a support, though still on the same side of the centre. The abscissæ of the extremities of this portion being  $\xi_1$  and  $\xi_2$ , the corresponding position of the support is given by

$$a = \xi_1 + \{ (l - \xi_1)^3 - (l - \xi_2)^3 \}^{\frac{1}{3}} (3l)^{-\frac{1}{3}}, \quad \dots \quad (84)$$

$$\text{or} \quad b = \eta_1 - (\eta_1^3 - \eta_2^3)^{\frac{1}{3}} (3l)^{-\frac{1}{3}}, \quad \dots \quad (84')$$

$$\text{where} \quad b = l - a, \quad \eta_1 = l - \xi_1, \quad \eta_2 = l - \xi_2.$$

These results have a real significance only when  $a/l$  exceeds  $0\cdot 5505$ .

We can also in cases (ii.), (iii.), and (iv.), have unchangeability of length in an asymmetrical portion which includes the centre.

Supposing the abscissæ of the two extremities  $\xi_1$  and  $-\xi_2$ , we require the values of  $dy/dx$  answering to  $+\xi_1$  and  $+\xi_2$



to be equal and opposite in sign. The points answering to  $+\xi_1$  and  $+\xi_2$  must thus lie on opposite sides of the "summit," where the slope vanishes.

Supposing  $\xi_2$  larger than  $\xi_1$ , then in case (ii.)  $\xi_1$  must be less than  $a$ , while in case (iii.)  $\xi_2$  must exceed  $a$ ; in case (iv.) both  $\xi_1$  and  $\xi_2$  must exceed  $a$ . The position of the support is easily found; thus when  $\xi_1$  and  $\xi_2$  are both to exceed  $a$  we find

$$a/l = \sqrt{\{2 - (\eta_1/l)^2 - (\eta_2/l)^2\}/6}, \quad . \quad . \quad (85)$$

where  $\eta_1$  (or  $l - \xi_1$ ) and  $\eta_2$  (or  $l - \xi_2$ ) are the distances of the ends of the asymmetrical portion from the two ends of the bar.

#### *Bar under additional weight.*

§ 26. In dealing with the bending of a bar under its own weight we have assumed it homogeneous, and of uniform section, and symmetrically supported. By having the supports unsymmetrical one could obtain unchangeability of length in an infinite variety of ways, but to discuss this fully would require more space than the practical importance of the subject seems to warrant. Before passing, however, to the practical applications, there is one point requiring notice. A bar not infrequently has to carry a weight additional to its own. For instance, the deflexion-bar of a magnetometer supports a magnet and its carriage on one arm, and unless clamped it carries, or at all events should carry, a counterpoise on the other arm. It is thus desirable to investigate the additional bending due to this cause. We shall suppose symmetry as before, the weight carried on one side of the centre being  $W$ , and its distance from the centre  $c$ . As before,  $O$  represents the centre,  $A$  the support,  $B$  the end of the rod; also  $C$  denotes the position of the weight. The notation used is the same as in § 21. The results given by the Bernoulli-Euler method are as follows, it being assumed that  $C$  lies between  $A$  and  $B$ :

Between  $O$  and  $A$ ,

$$y/(\frac{1}{2}x^2) = \frac{dy}{dx}/(x) = \frac{d^2y}{dx^2} = (W/E\omega\kappa^2)(c-a). \quad . \quad (86)$$

Between A and C,

$$\left. \begin{aligned} y &= (W/E\omega\kappa^2)\frac{1}{6}(a^3 - 3a^2x + 3cx^2 - x^3), \\ dy/dx &= (W/E\omega\kappa^2)\frac{1}{2}(-a^2 + 2cx - x^2), \\ d^2y/dx^2 &= (W/E\omega\kappa^2)(c - x). \end{aligned} \right\} \quad . \quad (87)$$

Between C and B,

$$\left. \begin{aligned} y &= (W/E\omega\kappa^2)\frac{1}{6}\{a^3 - c^3 + 3(c^2 - a^2)x\}, \\ dy/dx &= (W/E\omega\kappa^2)\frac{1}{2}(c^2 - a^2), \\ d^2y/dx^2 &= 0. \end{aligned} \right\} \quad . \quad (88)$$

To take account of the rod's own weight, we simply add the values of  $y$  &c. given in (69) or (70) to the corresponding values given above.

If the weight  $W$  were between the centre and the support, (86) would apply to the portion of the rod between the centre and the weight, while (88) would apply to the portion between the support and the end. For the portion between the weight  $C$  and the support  $A$  we should have

$$\left. \begin{aligned} y &= -(W/E\omega\kappa^2)\frac{1}{6}(3ac^2 - x^3 - 3c^2x + c^3), \\ dy/dx &= -(W/E\omega\kappa^2)\frac{1}{2}(2ax - x^2 - c^2), \\ d^2y/dx^2 &= -(W/E\omega\kappa^2)(a - x). \end{aligned} \right\} \quad . \quad (89)$$

In these last equations  $c$  is less than  $a$ . Equations (89) are deducible from equations (87) by altering the sign of  $W$  and interchanging  $a$  and  $c$ . We have spoken of  $W$  as a *weight* depending from the bar. By supposing  $W$  negative, however, we have the effect of an upward pull, relieving part of the weight of the bar. We may suppose this obtained from a belt passing over a pulley fixed above the bar.

§ 27. By the use of symmetrical auxiliary weights, we can without altering the position of the supports vary the portion of the bar whose length is unaffected by bending. Suppose, for instance, the bar carried by rollers in the position answering to  $a/l = 1/\sqrt{3}$ , for which the total length is unaffected when the bar is unloaded. Then to secure that a symmetrical central portion  $2b$  shall have its length unaffected, we select the auxiliary weights and their position so that one

of the following three equations holds :—

$$W(c-a) + w\{\frac{1}{2}l^2 - al + \frac{1}{6}b^2\} = 0, \quad . \quad . \quad . \quad . \quad . \quad (90)$$

$$W(-a^2 + 2cb - b^2) + \frac{w}{3}\{l(l^2 - 3a^2) - (l-b)^3\} = 0, \quad (91)$$

$$W(c^2 - a^2) + \frac{w}{3}\{l(l^2 - 3a^2) - (l-b)^3\} = 0. \quad . \quad . \quad (92)$$

The first equation will apply when  $b < a$ , or the end of the unaffected portion lies between the centre of the bar and the support; similarly the second equation applies when  $c > b > a$ , and the third when  $b > c$ . In all three cases we have supposed  $c > a$ . Under certain circumstances it might be necessary to have  $W$  negative, *i. e.* to have not a weight but an upward pull from a belt.

Suppose, as a particular case, that the auxiliary weight is applied at the end, and that  $a^2 = l^2/3$ , so that the bar when unweighted has its whole length unaffected by bending. The relations then are :—

for  $b > a (> l \times 0.5774)$ ,

$$W = w(l-b)^3 \div \{2l^2 - 3(l-b)^2\}; \quad . \quad . \quad . \quad (93)$$

for  $b < a$ ,

$$W = w\{(2\sqrt{3}-3)l^2 - b^2\} \div \{(6-2\sqrt{3})l\}. \quad (94)$$

In both these cases the value of  $W$  is always positive.

As a second example suppose that the bar is supported at its centre so that  $a=0$ . We then find from (91) and (92)

$$W = -\frac{1}{3}w\{l^3 - (l-b)^3\} \div \{c^2 - (c-b)^2\}. \quad (95)$$

or

$$W = -\frac{1}{3}w\{l^3 - (l-b)^3\} + c^2, \quad . \quad . \quad . \quad (96)$$

according as  $c$  is greater or less than  $b$ .

In both instances  $W$  is negative and so represents an upward pull. If this pull is applied at the extreme end of the bar we have

$$-W = \frac{1}{3}wl\{1 - (1-b/l)^3\} \div \{1 - (1-b/l)^2\}; \quad (97)$$

so that the pull ( $-W$ ) increases from  $(wl/3)$  to  $(wl/2)$ , as the portion of the bar to have its length unaffected is reduced from being the whole length to being an infinitesimal length at the centre.

*Numerical Applications to Standards of Length.*

§ 28. To illustrate the numerical application of the results in §§ 19 to 27 we shall consider the types of bars shown in fig. 1. Particulars as to the dimensions &c. of the bars are given in Table I. The data as to the types B and C are from the papers by Broch & Benoit already referred to. The dimensions of A, D, and E are from measurements of bars in the National Physical Laboratory. In the case of these bars, and to some extent in the bars B and C, the values ascribed to Young's modulus and the density are derived not from actual experiments on particular standards but from records of mean values for the materials of which the standards are composed. The letters have the meanings assigned in § 21.

TABLE I.

Types of Bars .....	A.	B.	C.	D.	E.
$\omega$ (cm. <sup>2</sup> ) .....	5·226	1·509	2·771	1·087	1·383
$\omega\kappa^2$ (cm. <sup>4</sup> ) .....	·782	·5213	·9832	·3805	·685
E (grammes wt. per cm. <sup>3</sup> ) .....	$9 \times 10^3$	$214 \times 10^7$	$925 \times 10^8$	$9 \times 10^4$	$9 \times 10^4$
$w$ (grammes) .....	44·4	32·35	24·71	9·24	11·76
$\rho$ .....	8·5	21·5	8·9	8·5	8·5
$l$ (cm.) .....	52·26	51·0	50·46	61·0	45·0
H (=height of C.G. above supports) (cm.) .....	0·67	1·00	1·118	1·025	1·075
$h$ (=height of divided surface above C.G.) (cm.) ...	0·67	0·00	0·882	5·0	6·8
$(wl^3/E\omega\kappa^2) \times 10^3$ .....	9·00	3·847	3·491	6·12	1·74
$(wl^3/E\omega\kappa^2)^2 \times 10^5$ .....	8·11	1·480	1·219	3·75	0·305

In Table I. I have taken for E the value given by Broch. The value quoted by Benoit, apparently for the same metres, is somewhat less, viz.  $197 \times 10^7$ . Calling a bar of type B but of this lower value of Young's modulus  $B'$ , the values of  $10^3(wl^3/E\omega\kappa^2)$  and of  $10^5(wl^3/E\omega\kappa^2)^2$  for  $B'$  are respectively 4·179 and 1·746.

§ 29. Table II.—calculated from (67) and (68)—gives the increment in the length of bars of the several types due respectively to an increase of 1 atmosphere in the surrounding pressure, and to the reaction of the supports when the bars are in air. The minus sign denotes shortening. The values of Poisson's ratio being unknown,  $\eta$  is tentatively given the values  $1/4$  and  $1/3$ .

TABLE II. (Unit = 0.001 mm.  $\equiv$  1  $\mu$ .)

Change of length of bar due to	Types.					
	A.	B.	B'.	C.	D.	E.
1 atmosphere { $\eta = \cdot 25 \dots$ pressure.     { $\eta = \cdot 3 \dots$	-0.60	-0.25	-0.27	-0.56	-0.70	-0.52
	-0.40	-0.16	-0.18	-0.38	-0.47	-0.35
reaction of { $\eta = \cdot 25 \dots$ supports.    { $\eta = \cdot 3 \dots$	+0.017	+0.026	+0.028	+0.027	+0.030	.....
	+0.022	+0.034	+0.037	+0.036	+0.039	.....

In the publications of the Bureau International lengths of standard metres seem usually recorded to 0.01  $\mu$  and occasionally to 0.001  $\mu$ . Benoit, however (*l. c.* p. 81), says: "l'erreur probable de la détermination d'une règle par rapport au Prototype international . . . a été trouvé de  $\pm 0.04 \mu$ ." As he is speaking of the highest class of metres, and admits an additional source of uncertainty in temperature corrections, it would appear that quantities of the order 0.004  $\mu$  possess as yet hardly a practical significance. Thus the influence of the reaction of the supports in the above types of bars possesses as yet only theoretical interest.

The influence of barometric pressure stands on a somewhat different footing. The departure of the barometric pressure at a station from its mean value will seldom, it is true, exceed 7/100 of an atmosphere; but the effects of a change of pressure of even this amount are shown by the table to be comparable with 0.04  $\mu$ . Supposing a standard measure to be in use at a high level Observatory, the decrease of the pressure from that at sea-level would merit closer attention, and the same remark is true to a much greater degree in

the case of a standard subjected to artificial pressures of many atmospheres.

§ 30. We have seen in § 22 that the length of a supported bar measured along the arc exceeds its horizontal projection to an extent given by the formula

$$2(s_1 - l)/l = (wl^3/E\omega\kappa^2)^2 f(a/l), \quad \dots \quad (98)$$

where

$$f(a/l) = \frac{1}{36} - \frac{1}{8}(a/l)^2 + \frac{7}{24}(a/l)^4 - \frac{2}{15}(a/l)^6 + \frac{1}{360}(a/l)^8. \quad (99)$$

For values of  $a/l$  between 0 and 1, Broch (*l. c.*) has shown that  $f(a/l)$  has no maximum and only one minimum. The minimum answers to  $a/l = .5594$  approx. (more exactly (Broch, *l. c.* p. B. 67)  $.559380119$ ). The following are approximate values for  $f(a/l) \times 10^5$  :—

$$\begin{array}{cccccccc} a/l = & 0 & 0.25 & 0.5 & 0.5594 & 0.5774 & 0.6 & 0.75 & 1.0. \\ 10^5 \times f(a/l) = & 1786 & 1105 & 71 & 8 & 15 & 260 & 868 & 5397 \end{array}$$

The smallness of  $f(a/l)$  when  $a/l$  lies between 0.5 and 0.5774 is specially noteworthy.

Table III. gives the difference between the entire length  $2l$  and its horizontal projection for specified positions of the supports.

TABLE III.

Excess of arc over chord, unity  $\equiv 1\mu \equiv 0.001$  mm.

Value of $a/l$ .	Type of bar. } A.	B.	B'.	C.	D.
0	.757	.135	.159	.110	.409
0.5	.0301	.0054	.0063	.0044	.0162
0.5594	.0034	.0006	.0007	.0005	.0018
0.5774	.0064	.0011	.0013	.0009	.0034
0.6	.110	.020	.023	.016	.039
1.0	2.287	.407	.481	.332	1.235

Broch (*l.c.p.* B. 70) finds for the minimum difference between chord and arc in the type B the value  $\cdot 0003 \mu$ , or only half that given above for the case  $a/l = 0\cdot 5594$ . This is not due to his retaining 9 instead of 4 figures in the critical value of  $a/l$ , but to his use of  $\cdot 7486$  as the value of  $\omega \kappa^2$  instead of  $\cdot 5213$  as given in Table I. For this I see no justification. He agrees with Benoit in recording  $\cdot 5213$  as the value of  $\omega \kappa^2$  for bending about a horizontal diameter (*i.e.* in a vertical plane); and even if he were correct in quoting  $\cdot 7486$  (Benoit gives  $\cdot 5444$ , which looks more probable) as the value of  $\omega \kappa^2$  for bending about a *vertical* axis, the result would not apply to the actual problem. This discrepancy, however, hardly affects the conclusion drawn by Broch, that the difference between chord and arc is negligible for metre prototypes supported so that  $a/l = 0\cdot 55938$ . At the same time, Table III. shows that a comparatively small departure of  $a/l$  from the best position suffices to increase the difference between arc and chord tenfold, and for measurements of the highest accuracy the point should be borne in mind. The rapid increase in the difference between chord and arc as the supports are moved out to near the ends is specially notable.

§ 31. The absolute difference between the arc and its horizontal projection is greater for the entire length than for any shorter portion; but the relative difference—*i.e.* the difference per unit length—is considerably greater for some short portions. The relative difference is greatest where the slope is greatest, its largest value being the maximum value of

$$(ds/dx - 1) \text{ or } \frac{1}{2}(dy/dx)^2.$$

We have seen in § 24 that the largest value of  $dy/dx$  occurs either at the end of the bar or at  $x = x_1$ , where  $x_1$  is given by (76); and equations (77) and (79) supply the values of  $dy/dx$  at these two points. From these we find the corresponding values of  $(ds/dx - 1)$  given in Table IV. Of the numerical results given, those not in brackets are the absolutely largest values met with throughout the bar. To avoid decimals as much as possible the factor  $10^9$  has been applied.

TABLE IV.

Largest values of  $10^9 \times (ds/dx - 1)$ .

Bar.	Value of $x$ .	$a/l = 0$	$\cdot 2$	$\cdot 4$	$\cdot 5$	$\cdot 5$	$\cdot 5774$	$\cdot 6$	$\cdot 8$	$1\cdot 0$
A	$\left\{ \begin{smallmatrix} x_1 \\ l \end{smallmatrix} \dots \right.$	1126	872	305	$\begin{smallmatrix} [0] \\ 70 \end{smallmatrix}$	$\begin{smallmatrix} 6 \\ 6 \end{smallmatrix}$	$\begin{smallmatrix} 17 \\ [0] \end{smallmatrix}$	$\begin{smallmatrix} 36 \\ [7] \end{smallmatrix}$	$\begin{smallmatrix} 973 \\ [953] \end{smallmatrix}$	$\begin{smallmatrix} 4504 \\ 4504 \end{smallmatrix}$
B	$\left\{ \begin{smallmatrix} x_1 \\ l \end{smallmatrix} \dots \right.$	206	159	56	$\begin{smallmatrix} [0] \\ 13 \end{smallmatrix}$	$\begin{smallmatrix} 1\cdot 1 \\ 1\cdot 1 \end{smallmatrix}$	$\begin{smallmatrix} 3\cdot 0 \\ [0] \end{smallmatrix}$	$\begin{smallmatrix} 7 \\ [1\cdot 3] \end{smallmatrix}$	$\begin{smallmatrix} 178 \\ [174] \end{smallmatrix}$	$\begin{smallmatrix} 822 \\ 822 \end{smallmatrix}$
B'	$\left\{ \begin{smallmatrix} x_1 \\ l \end{smallmatrix} \dots \right.$	242	188	66	$\begin{smallmatrix} [0] \\ 15 \end{smallmatrix}$	$\begin{smallmatrix} 1\cdot 3 \\ 1\cdot 3 \end{smallmatrix}$	$\begin{smallmatrix} 3\cdot 6 \\ [0] \end{smallmatrix}$	$\begin{smallmatrix} 8 \\ [1\cdot 5] \end{smallmatrix}$	$\begin{smallmatrix} 210 \\ [205] \end{smallmatrix}$	$\begin{smallmatrix} 970 \\ 970 \end{smallmatrix}$
C	$\left\{ \begin{smallmatrix} x_1 \\ l \end{smallmatrix} \dots \right.$	169	131	46	$\begin{smallmatrix} [0] \\ 11 \end{smallmatrix}$	$\begin{smallmatrix} 0\cdot 9 \\ 0\cdot 9 \end{smallmatrix}$	$\begin{smallmatrix} 2\cdot 5 \\ [0] \end{smallmatrix}$	$\begin{smallmatrix} 5 \\ [1\cdot 1] \end{smallmatrix}$	$\begin{smallmatrix} 146 \\ [143] \end{smallmatrix}$	$\begin{smallmatrix} 677 \\ 677 \end{smallmatrix}$

A is the only bar of the four in which the difference between a short arc and its horizontal projection can exceed one part in a million. So far as Table IV. is concerned, the standard yard compares unfavourably with modern types.

§ 32. As the angle of slope may be more easily grasped than the difference between the arc and its horizontal projection, I give in Table V. below the particulars as to the slope corresponding to the data in Table IV. A plus sign means that the slope is downwards in the direction of  $x$  increasing, or towards the end of the bar, a minus sign implies the reverse. To avoid decimals the angles are measured in seconds.

TABLE V.—Largest values of slopes.

Bar.	Value of $x$ .	$a/l = 0$	$\cdot 2$	$\cdot 4$	$\cdot 5$	$\cdot 5$	$\cdot 5774$	$\cdot 6$	$\cdot 8$	$1\cdot 0$
A	$\left\{ \begin{smallmatrix} x_1 \\ l \end{smallmatrix} \dots \right.$	"	"	"	$\begin{smallmatrix} [0] \\ +77 \end{smallmatrix}$	$\begin{smallmatrix} -23 \\ +23 \end{smallmatrix}$	$\begin{smallmatrix} -38 \\ [0] \end{smallmatrix}$	$\begin{smallmatrix} -55 \\ [-25] \end{smallmatrix}$	$\begin{smallmatrix} -283 \\ [-285] \end{smallmatrix}$	$\begin{smallmatrix} -619 \\ -619 \end{smallmatrix}$
B	$\left\{ \begin{smallmatrix} x_1 \\ l \end{smallmatrix} \dots \right.$	+132	+116	+69	$\begin{smallmatrix} [0] \\ +33 \end{smallmatrix}$	$\begin{smallmatrix} -10 \\ +10 \end{smallmatrix}$	$\begin{smallmatrix} -16 \\ [0] \end{smallmatrix}$	$\begin{smallmatrix} -24 \\ [-11] \end{smallmatrix}$	$\begin{smallmatrix} -123 \\ [-122] \end{smallmatrix}$	$\begin{smallmatrix} -264 \\ -264 \end{smallmatrix}$
B'	$\left\{ \begin{smallmatrix} x_1 \\ l \end{smallmatrix} \dots \right.$	+144	+126	+75	$\begin{smallmatrix} [0] \\ +36 \end{smallmatrix}$	$\begin{smallmatrix} -11 \\ +11 \end{smallmatrix}$	$\begin{smallmatrix} -17 \\ [0] \end{smallmatrix}$	$\begin{smallmatrix} -26 \\ [-12] \end{smallmatrix}$	$\begin{smallmatrix} -134 \\ [-132] \end{smallmatrix}$	$\begin{smallmatrix} -287 \\ -287 \end{smallmatrix}$
	$\left\{ \begin{smallmatrix} x_1 \\ l \end{smallmatrix} \dots \right.$	+120	+106	+62	$\begin{smallmatrix} [0] \\ +30 \end{smallmatrix}$	$\begin{smallmatrix} -9 \\ +9 \end{smallmatrix}$	$\begin{smallmatrix} -15 \\ [0] \end{smallmatrix}$	$\begin{smallmatrix} -21 \\ [-10] \end{smallmatrix}$	$\begin{smallmatrix} -112 \\ [-110] \end{smallmatrix}$	$\begin{smallmatrix} -240 \\ -240 \end{smallmatrix}$



For the value  $\cdot 5$  of  $a/l$  the slopes at the end and at  $x=x_1$  are always numerically equal but of opposite sign.

Also, as may be seen from formula (79), the slope at the end, numerically considered, is exactly twice as great when the bar is supported at the ends as when it is supported at the middle.

Even in bar C the slope at the ends changes (algebraically) to the extent of  $6'$  as the supports are moved from under the centre to under the ends.

§ 33. Table VI. gives for some of the typical bars the values of  $x_1/l$  and of  $x_1$ —i. e. the distance from the centre of the points where the largest slope is found—for representative values of  $a/l$ .

TABLE VI.  
Values of  $x_1/l$ , and also of  $x_1$  (in centimetres).

		$a/l = \cdot 5$	$\sqrt{1/3}$	$\cdot 6$	$\cdot 8$	$1\cdot 0$
Bar.	$x_1/l =$	$\cdot 3333$	$\cdot 3933$	$\cdot 4472$	$\cdot 7746$	$1\cdot 0$
A.	$x_1 =$	$17\cdot 42$	$20\cdot 56$	$23\cdot 37$	$40\cdot 48$	$52\cdot 28$
B & B'.	$x_1 =$	$17\cdot 00$	$20\cdot 06$	$22\cdot 81$	$39\cdot 51$	$51\cdot 00$
C.	$x_1 =$	$16\cdot 82$	$19\cdot 85$	$22\cdot 57$	$39\cdot 09$	$50\cdot 46$
D.	$x_1 =$	$20\cdot 33$	$23\cdot 99$	$27\cdot 28$	$47\cdot 25$	$61\cdot 0$

When  $a/l$  is less than  $\cdot 5$  the greatest slope, it will be remembered, is found at the end of the bar.

§ 34. In the metre prototypes B or B' the divisions occur on the neutral surface, and on the Bernoulli-Euler theory their distance apart is unaffected by stretching of the material. In the other types, stretching is a much more important factor than the difference between the arc and its horizontal projection. As shown in § 22, the stretching in any symmetrical central portion of a "fibre" in the upper half of the cross section is  $2h dy/dx$ , where  $h$  is the height of the "fibre" considered above the C.G. of the section, and  $dy/dx$  is the tangent of slope at one end of the portion considered. When  $a/l$  is less than  $0\cdot 5$  the stretching is greater for the

whole length of the bar than for any shorter symmetrical part; when, however,  $a/l$  exceeds  $0\cdot5$  the stretching is less for the whole than for the central length  $2x_1$ , for which it is a maximum.

Table VII. gives the stretching in the divided upper surface for the whole length  $2l$ , as well as for the central portion  $2x_1$ . The sign is + or - according as the upper surface is lengthened or contracted.

TABLE VII.

Stretching of upper (divided) surface (unity =  $1\mu \equiv 0\cdot001$  mm.).

Bar.	Length considered.	$a/l=0$ .	$\cdot 2$ .	$\cdot 4$ .	$\cdot 5$ .	$\cdot 5$ .	$\sqrt{1/3}$ .	$\cdot 6$ .	$\cdot 8$ .	$1\cdot 0$
A.	$2l$ .....	+20·11	+17·70	+10·46	+5·03	+1·49	·00	-1·61	-18·50	-40·22
	$2x_1$ .....	.....	.....	.....	·00	-1·49	-2·45	-3·60	-18·69	-40·22
C.	$2l$ .....	+10·26	+ 9·03	+ 5·34	+2·57	+0·76	·00	-0·82	- 9·44	-20·53
	$2x_1$ .....	.....	.....	.....	·00	-0·76	-1·25	-1·84	- 9·54	-20·53

The values of  $x_1$  will be found in Table VI.

As an illustration, take the case of bar A when  $a/l=0\cdot6$ .

Between the centre and the point  $x=x_1(=23\cdot37$  cm.) the upper surface is all contracted, the total shortening in this portion amounting to  $\frac{1}{2}$  of  $3\cdot60$  or  $1\cdot8\mu$ . Between  $x=x_1$  and  $x=l$ , i. e. in the  $28\cdot89$  cm. nearest the end, the upper surface is all extended, the total lengthening in this portion amounting to  $1\cdot0\mu$ . Thus in the entire half length of  $52\cdot26$  cm. there is a shortening of  $0\cdot8\mu$  in the upper surface.

When  $a/l=\sqrt{1/3}$ , the contraction of the upper surface between  $x=0$  and  $x=x_1$  is exactly balanced by the extension between  $x=x_1$  and  $x=l$ ; the fact, however, remains that there is appreciable shortening of one part of the upper surface and appreciable lengthening of another. Even in the bar C when  $a/l=\sqrt{1/3}$  we have in the central  $2x_1$ , or  $39\cdot7$  cm., a shortening of  $1\cdot25\mu$ .

If our object is to ensure that the numerically greater of the two changes, contraction of the central portion and extension of the terminal portions, shall be a minimum, then

we must select not  $\sqrt{1/3}$  but  $0\cdot5$  as the value of  $a/l$ . For  $a/l=0\cdot5$  we have  $x_1=l/3$ ; thus, if the bar be supposed divided into three equal portions, the central portion has its upper surface all under contraction, while the two end portions have their upper surfaces all under extension. Further, the total shortening of the upper fibre in the central portion is exactly equal to the total lengthening of the upper fibre in either of the end portions.

The mathematical equivalent to this physical property is the fact that for the value  $0\cdot5$  of  $a/l$  the slope at the end is exactly equal but opposite to the slope at the point  $x=l/3$ .

Another interesting fact is that when  $a/l=0\cdot5$  the point other than the centre where the tangent is horizontal is given by

$$x_3/l=1/\sqrt{3}.$$

§ 35. As illustrating some of the other results, we may take the case of the Kew standard yard. The actual yard length refers to the distance between the centres of two gold plugs let into the bar so that they lie flush with the upper surface. These plugs are not at exactly equal distances from their respective ends, but the difference in the distances may be neglected for our present purpose; so that we may treat the distance between the plug centres as representing a central portion 91·44 cm. long in a bar 104·52 cm. long. To keep this length unstretched we must select for  $a/l$  a value such that  $x_3$  in (75) is 45·72, while  $l$  is 52·26. The answer to this problem will be found to be

$$a/l=0\cdot5768, \text{ or } a=30\cdot14 \text{ cm.}$$

Again, the Kew standard yard has its upper surface graduated into 40 inches, the inch numbered 0 being approximately 1·55 cm. from one end of the bar, and the inch numbered 36 about 11·53 cm. from the other end. To secure that the yard 0 to 36 inches shall be unaffected by stretching, we determine  $a/l$  from (85), substituting 1·55 for  $\eta_1$ , 11·53 for  $\eta_2$ , and 52·26 for  $l$ . In this way we find

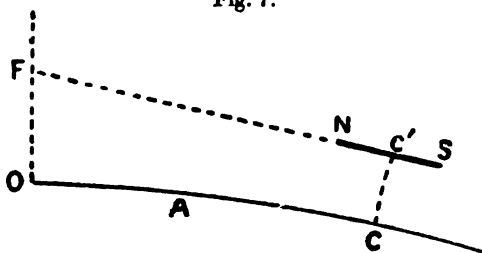
$$a/l=0\cdot5765, \text{ or } a=30\cdot125 \text{ cm.}$$

The interval between the two supports is approximately only 0·03 cm. less in the second instance than in the first.

*Application to Deflexion-Bars of Magnetometers.*

§ 36. In A, B, B', and C it is the length of the bar itself that has to be considered. D and E are representatives of a different class. They serve to support a carriage holding a magnet. The carriage may have a groove fitting on the bar, or a projecting pin fitting in one of a series of holes in the upper surface. In either case, supposing the adjustment perfect and the bar strictly horizontal, the centre of the magnet—which is the fundamental point—will be vertically over a certain graduation on the bar, and at a constant height  $h$  above the neutral plane. In actual use, however, the bar bends under its own weight and that of the magnet and carriage combined. This is illustrated diagrammatically in fig. 7, supposed to be a vertical section containing the

Fig. 7.



magnetic axis NS and the line of centres OAC of the bar. The arrangements are such that NS is parallel to the tangent at C, while the normal at C passes through C' the centre of the magnet. F in fig. 7 represents the centre of a second magnet whose suspension is vertically over O, and whose height is altered until F appears central, as seen through a sighting-tube, temporarily substituted for NS. The magnetic reductions suppose NS horizontal, in the same horizontal plane with F, and at a distance from it equal to OAC, or  $c$ . In reality NS is inclined to the horizon at an angle  $\tan^{-1}(dy/dx)_{x=c}$ ; and if we suppose—which is not strictly true—that the sighting-tube is as heavy as the magnet, the true distance of C' from F is not  $c$  but

$$c\{1 + \frac{1}{2}(dy/dx)^2_{x=c}\} + h(dy/dx)_{x=c}.$$

The bar D rests throughout its central 29 cms. on a horizontal plate, to which it is bolted at two points each 14 cm.

rom the centre \*. Thus the half on one side of the centre is practically a rod of 61—14, or 47, cms. length, clamped at one end so that  $y$  and  $dy/dx$  vanish with  $x$ . The bending and stretching are thus the same as in the half of a bar 94 cms. long supported at its centre.

The bar E rests on horizontal pins which pass through two holes drilled through the bar at the level of its neutral line. It may thus be regarded as supported, the distance of the supports from the centre being half the distance (6 cm.) between the pins. Consequently for E we have  $l=45$ ,  $a=3$ . The magnet with its carriage weighs approximately 122 grammes in the case of D, and 390 grammes in the case of E.

Commonly the magnet is used at two fixed distances, its centre being either 30 or 40 cms. from the centre of the bar. What we want to know in the present case is the slope at the particular point where the additional weight acts. As already explained, this is the precise point where the Bernoulli-Euler results are likely to be least exact; still, the uncertainty is hardly likely to be serious. Employing the values given for  $\omega$ , &c. in Table I., I find the following data for the slope and for the quantities on which the distance C'F in fig. 7 depends :—

TABLE VIII.

Magnet at .....	Bar D.		Bar E.	
	30 cm.	40 cm.	30 cm.	40 cm.
Angle of slope of magnet=	78"	113"	115"	163"
$h \, dy/dx$ (cms.)=	·00189	·00273	·00379	·00537
$\frac{1}{2}c \, (dy/dx)^2$ (cms.)=	$2 \times 10^{-6}$	$6 \times 10^{-6}$	$5 \times 10^{-6}$	$13 \times 10^{-6}$

§ 37. So far as concerns the effect on the magnetic observations, the departure of the magnetic axis from horizontality is negligible, and the value of  $(c/2)(dy/dx)^2$  is wholly insignificant. It is otherwise, however, with  $h \, dy/dx$ , especially in the case of bar E, where the error introduced is almost

\* The D section is the common one, but the above clamping arrangements are peculiar to the old Kew standard. In modern English magnetometers the bars are all supported.

exactly twice as great as with D. In both bars the value of  $hdy/dx$  varies pretty closely as the distance  $c$ . This is so far fortunate, as it minimises the indirect effect on a certain correction supplied by magnetic theory, whose accuracy is sensitive to errors in the assumed values of the distances between the deflecting and deflected magnets.

To calculate the direct effect on the calculated value  $X$  of the horizontal magnetic component we may employ the formula

$$X^2 = Nr^{-3},$$

where  $N$  is a function of certain observed quantities, including time of vibration and sine of deflexion-angle, while  $r$  is the distance between the centres of the two magnets. The correction  $\delta X$  to  $X$ , necessitated by a correction  $\delta r$  to the received value of  $r$ , is given by

$$2\delta X/X = -3\delta r/r.$$

For bar E, on the average of the results at 30 and 40 cms., we have

$$\delta r/r = +.00013,$$

whence

$$\delta X/X = -.000195.$$

At London, where  $X = .184$  c.g.s. approximately at present, this would give

$$\delta X = -.000036 \text{ c.g.s.}$$

Near the magnetic equator—*e.g.* in parts of India— $X$  is twice as large as in London, so that the *error* introduced by the flexure of bar E under gravity might attain to  $+.00007$  c.g.s. As it is usual to attempt to measure  $X$ —or at least to record its value—to  $.00001$  c.g.s., the source of error now indicated possesses more than merely theoretical interest\*.

#### *Concluding Remarks.*

§ 38. A common remark applies to all our investigations into the effects of flexure on length. So long as a bar is always used at a fixed station, in one exactly specified way, and its length is measured, or defined as holding, under the exact conditions of use, it is immaterial whether flexure

[\* *March 1902.*—Direct experiments made on bars of D and E sections at the National Physical Laboratory having confirmed the theory of § 37 for supported bars, the effect of bending is now regularly observed and allowed for in the tables of constants supplied there to magnetometers.]

affects its length or not. If a standard yard, for instance, is supported in an absolutely uniform way on rollers, the mere fact that the distance between the centres of the gold plugs would be altered by shifting the rollers cannot be said to constitute an unmistakable mark of its inferiority as compared to the Bureau International's type B. There may, however, be practical objections to particular forms of standards of lengths, and to particular positions of the supports. It is undesirable, for instance, that a small accidental variation in the position of the supports should appreciably affect the length. Thus in the case of a standard yard the ends of the bar seem a much less advisable position for the supports than the points answering to  $a/l = \sqrt{1/3}$ . This, of course, has been recognized since Airy's time. Again, the type B has, at least theoretically, the conspicuous advantage that even large variations in the position of the supports are of secondary importance. It is not, of course, impossible that there may be some compensating disadvantages, apart from mere expense or difficulty of construction. In a bar of rectangular section there would seem less grounds for fearing difference in elastic property or density between the material above and below the neutral plane than in a bar of unsymmetrical section like B or C. In the event of differences of elasticity between the material in the flange and in the upper and lower limbs, the plane of unstretched fibres might not coincide with the horizontal plane through the line of centres. If heterogeneity of this kind existed to any appreciable extent, it would militate against the advantages claimed for the type B.

#### DISCUSSION.

Prof. EVERETT congratulated the author upon the practical application of a difficult theory to the measurements of lengths and volumes.

Mr. WATSON said that it was usual in deducing the radius of a coil from the measurement of its circumference with a steel tape to diminish the result by half the thickness of the tape. He would like to know if this was the right correction to apply. In measuring the circumference of a cylinder it is necessary to wind the tape in a spiral so as to bring the divisions side by side. This gives a result

which is too great and not too small, as might at first sight be imagined.

Mr. CAMPBELL asked if any special experiments (optical or otherwise) had been performed to determine directly the bending of standards at different points of their length?

Dr. LEHFELDT asked if the work of the author could be used to determine the pressure corrections of thermometers. He would like to ask why it was necessary to use two rigid supports instead of a number of slightly elastic ones.

Prof. THOMPSON said that the paper was important because of its bearing on the question of the relation between the units of different nations. He drew attention to the alteration of the factor converting metres into inches, and asked if it was due to alterations in the properties of matter or to errors of observation. The two legal definitions of the gallon differ by an appreciable amount, and it would be interesting to know if this discrepancy could be due to changes in the volume of measures due to the liquids contained by them.

Dr. CHREE, in reply to Mr. Watson, expressed some doubt as to whether a tape could be regarded as an isotropic elastic solid subject to the Bernouilli-Euler theory of beams; if the curvature were large the elastic limit might be exceeded unless the tape were very thin. In reply to Mr. Campbell, the author stated that experiments made at Sèvres on metre bars apparently agreed well with the Bernouilli-Euler theory. In reply to Dr. Lehfeldt, he said he had treated the subject of the external and internal pressure coefficients of thermometers in a paper published some years ago; the results of the present paper might throw some further light on the subject in the case where the bulbs were long and of cylindrical shape. With respect to a suggestion that it might be advantageous to support a standard of length on a large number of points, Dr. Chree said that Airy had treated this question mathematically many years ago; but that in practice there might be uncertainty as to the true distribution of pressure, just as in the case of support on a flat surface which was not a mathematical plane. In reply to the President, he said that the difference between the results of the recent and old comparisons of the yard and meter might be



partly due to the fact that the divisions on standard yards are somewhat coarse for measurements of the highest degree of accuracy; further, that something might be due to the fact that  $62^{\circ}$  F., not being defined in terms of any definite scale, the temperature accepted as standard for English measures of length might have slightly altered.

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II. *On the Variation with Temperature of the Thermoelectromotive Force, and of the Electric Resistance of Nickel, Iron, and Copper, between the Temperatures of  $-200^{\circ}$  and  $+1050^{\circ}$ . By E. PHILIP HARRISON, University College, London\*.*

THE main objects of the investigation which forms the subject of this paper are as follows :—

To trace over as wide a range as possible the change with temperature of the thermoelectromotive force and the resistance of Nickel and Iron, *using in all experiments the same specimens of metal*; to investigate any singularities that may be present in the curves representing the change; and to determine whether they occur at the same temperature in each of the curves. It was originally intended to investigate the magnetic properties of the same specimens, but time has not sufficed for this.

## SECTION I.

### THERMOELECTRIC PROPERTIES.

#### (1) *Results of Previous Observers.*

In his researches on thermoelectricity † Tait gives the results of some of his measurements for iron which extended from  $0^{\circ}$  to the melting-point. The second portion of his iron couple was either platinum or an alloy of platinum and iridium; he used mercury thermometers up to  $300^{\circ}$ , but did not correct for stem-exposure, and the experimental difficulties due to chemical action and the measurement of temperature made observations above  $500^{\circ}$  quite unreliable. His results

\* Read October 25, 1901.

† Proc. Roy. Soc. Edin. December 1873; 'Nature,' Rede Lecture, May 1st, 1873.

within a moderate range of temperature (obtained with the hot junction in an oil-bath) showed that the E.M.F. temperature-curves were made up of a series of "excellent parabolas." At higher temperatures "the parabola was slightly steeper on the hotter than on the colder side." He also found that between  $200^{\circ}$  and the melting-point, two or more distinct neutral points existed.

Professors Fleming and Dewar's experiments on the same subject \* extend from the temperature of boiling oxygen to  $100^{\circ}$  C. Their paper gives the experimental methods used and the numerical results, but a discussion of the latter is reserved by the authors for a further communication. The temperature of the "hot junction" in their experiments was measured by a platinum thermometer, and their results were expressed on the platinum scale.

Holborn and Day † compared a platinum-platinum-rhodium couple with the air-thermometer, and ‡ tested a number of similar couples, but were unable to obtain consistent results with oxidizable metals at high temperatures. They adopt Tait's method of representing their results by portions of parabolas for limited ranges of temperature.

Stansfield §, from observations on couples formed of platinum and platinum-iridium or platinum-rhodium alloys, found that for these couples the Peltier effect  $\left( T \frac{dE}{dt} \right)$  approximated closely to a linear function of the temperature, but that the thermoelectric power  $\left( \frac{dE}{dt} \right)$  could not be so represented.

#### DESCRIPTION OF APPARATUS.

##### A. *Measurement of E.M.F.*

An ordinary potentiometer method was used and the general arrangement of apparatus is shown in fig. 1. A two-metre bridge-wire BP was connected in series with a resistance-box R and a 1 ohm rheostat O. The P.D. due to the

\* Phil. Mag. 1895, vol. xl. pp. 95-119.

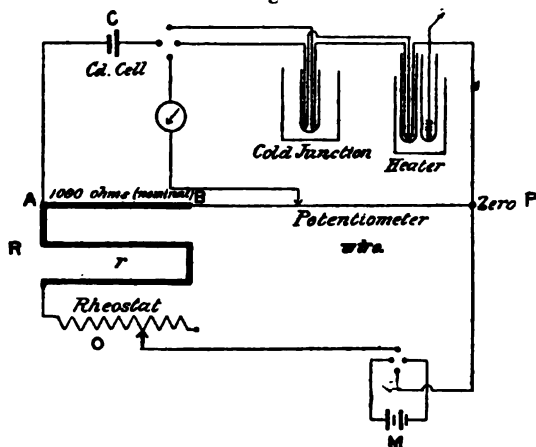
† Wiedemann's *Annalen*, August 1899.

‡ Berlin Academy, July 1900.

§ Phil. Mag. 1898, vol. xlviii.

thermo-couple was balanced against that due to two accumulators M. Before each reading of the E.M.F. of a thermo-couple the standard cadmium cell C\* was balanced on a definite resistance AB of the box by adjusting  $r$ , fine adjustment being made by the rheostat. Alterations in the E.M.F. of the cadmium cell with temperature were too small to affect the observations to 1 part in 1000. Since the iron-copper couple gives an E.M.F. about 10 times smaller in places than the nickel-copper, a shunt equivalent to  $1/9$  of the bridge-wire resistance was constructed, and arranged so that it could be inserted at will between the ends of the bridge-wire.

Fig. 1.



The bridge-wire was calibrated by the Carey Foster method. A galvanometer of the Wiedemann pattern was used with a pair of 1 ohm coils, and with the usual scale and telescope arrangement for reading deflexions. Thermoelectric effects at the slide-wire contact were avoided by always depressing the key with a glass cap. With the above arrangement of apparatus, the position of the key on the potentiometer-scale could be adjusted in the case of copper-nickel junction to the fifth of a millimetre, in the case of copper-iron junction to half a millimetre. Readings of E.M.F. of copper-nickel

\* E.M.F. 1019 millivolts.

couples were accurate to 1.8 microvolts, while those of copper-iron couples were accurate to less than 1 microvolt at moderate temperatures.

### B. *Measurement of Temperature.*

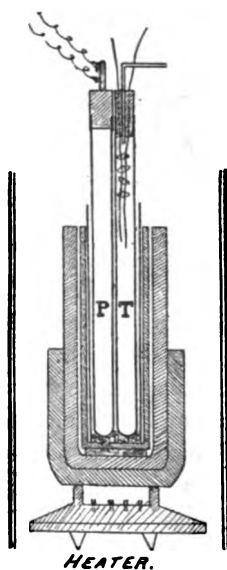
In all cases the hot-junction temperatures were measured by a platinum thermometer and recorded automatically by Callendar's Recorder, the advantage of this method being that simultaneous readings of E.M.F. and of temperature are obtained without the necessity for two observers. While the temperature was changing slowly (say  $\frac{1}{2}^{\circ}$  per minute) the readings at  $500^{\circ}$  were correct to  $1/10$  degree. Observations were taken in all cases with rising and falling temperatures in order to make sure that the "lag" of the thermometer or recorder did not introduce appreciable errors.

The heating-apparatus (fig. 2) consisted of several concentric iron cylinders closed at one end. For temperatures below  $700^{\circ}$  this arrangement was placed on a small Fletcher burner, and the whole surrounded by a cylinder of polished tin-plate large enough to leave an air-space of two or three cms. between itself and the iron heater. The inner wall of the "tin" cylinder was lined with  $\frac{1}{8}$  inch asbestos board.

For heating above  $700^{\circ}$  C. a Fletcher gas-furnace with an air draught was used, two dampers being arranged for regulating the temperature.

The hot junction formed by fusing together in a reducing blowpipe-flame the ends of the copper, nickel, and iron wires, was placed nearly at the bottom of a 12-inch porcelain tube of 9 mm. internal diameter. The platinum-thermometer tube was then placed by the side of the tube containing the couple, and the two

Fig. 2.



were bound together with several layers of thick sheet-copper, extending six inches from the bottom of the tubes, which were then placed in the heater and packed round with asbestos. The top of the heater was covered with 4 or 5 layers of asbestos-paper separated from one another by air-spaces.

The other ends of the nickel and iron wires were soldered to copper leads, and the junctions placed in very small glass tubes, which together with a mercury thermometer reading to  $1/10$  degree C. were placed in a large test-tube full of water, the test-tube itself being also immersed in water. This arrangement formed the cold junctions, and their temperature always varied with the temperature of the room. Every observation is reduced to cold junction at  $0^{\circ}$  C. by means of a separate series of observations applied graphically. Observations at the higher temperatures were taken first in each case, so that any change that might be caused by the heating would occur at the beginning of the experiments. Confirmatory observations were made in steam, aniline vapour, and sulphur vapour. In the case of steam an ordinary hypsometer was used, the couple-tube and pyrometer being placed in it simultaneously, and the temperature of the steam calculated as well as observed by the pyrometer. The aniline was boiled in a glass beaker about 2 ft. high, provided with "tin" plates at intervals up its length to prevent convection-currents. For the sulphur point an ordinary sulphur boiling-point apparatus was used.

The effect of heating the junctions in hydrogen and in carbon was tried in every case. A large rubber bag was filled with 96% hydrogen from a cylinder. The bag communicated with one arm of a three-way tap, the other two arms of which went to the pump and couple-tube respectively. The couple-tube was washed out with hydrogen by alternately exhausting the apparatus and letting in the gas, and observations were taken at pressures slightly in excess of atmospheric pressure. The hot junctions when packed in bone-black in the porcelain tube gave consistent results up to  $700^{\circ}$ , but quite inconsistent results above that temperature. Finally, in each case observations were taken in liquid air. The junctions were put naked into the liquid with the platinum

thermometer, also without its tube, beside them. Temperature of the air was recorded.

*Method of avoiding Oxidation.*

For observations above  $500^{\circ}$  it was necessary to protect the couples as far as possible from any gases that might chemically affect them. Owing to the difficulty of obtaining any argon at the time of the experiments, it was finally decided to use as good a vacuum as possible. The porcelain tube containing the junction was closed with a rubber cork through which a glass tube passed. The three wires were brought up between the cork and the sides of the tube, and were gently burnt into the former. Marine glue was melted and poured over the cork and top of the tube, which was then warmed till the glue ran into every hole. Finally a coating of beeswax was spread over the glue—a precaution which was found to be very necessary to the preservation of the vacuum, though as beeswax melts at a low temperature, the top of the hot-junction tube had to be kept well protected from the heat of the burner. The glass tube which passed out of the cork was then sealed directly on to a Fleuss pump. Two  $P_2O_5$  tubes were interposed between the porcelain tube and the pump, and a mercury gauge was set up with a barometer by its side for comparison. The wires above the hot junction were in the first instance insulated by being separately wrapped in several layers of asbestos-paper as far up as the mouth of the tube. Subsequently, the wires inside the tube were insulated by little circular mica disks instead of asbestos, because the latter was found to evolve gas on heating which contaminated the couples. With mica insulation no difficulty was found in keeping the vacuum as good as that above the barometer for several days.

*Regulation of the Temperature.*

It was thought possible that hysteresis occurred at the singular point of the nickel curve. To investigate whether or not this was the case, it was necessary to take observations with a very slowly-rising or slowly-falling temperature.

A special apparatus was constructed for regulating the gas-pressure, and for slowly turning on or off the gas-supply to the Fletcher burner. This apparatus worked very satisfactorily, although only a small hysteresis effect was detected, which is shown by the double line at the summit of difference-curve D (Ni) (fig. 4); the upper branch was obtained with rising, the lower one with falling temperature. The difference could not be explained by temperature-lag in either the thermometer or the couple.

#### *Method of taking the Observations.*

The temperature of the hot junction being steady, or changing not more than 1 degree in five minutes, a stop-watch was started when the pen of the Recorder was crossing a horizontal "time-line." The scale of the potentiometer was adjusted by reference to the cadmium-cell, and the latter was then cut out and the Cu-Ni couple switched into the galvanometer-circuit. Time on the stop-watch at which balance occurred, and the bridge-reading at balance being noted, as soon after each observation as possible the temperature of the cold junction was read to 1/10 degree. The same observations were repeated on the copper-iron junction with the bridge-wire shunted.

All temperatures are expressed as air-thermometer temperatures, correction from the platinum-scale being applied graphically by means of a difference-curve.

All E.M.F.'s are given in microvolts.

#### *Discussion of Results.*

The curves for variation of E.M.F. with temperature of copper-nickel and copper-iron couples might be roughly described as a straight line and a parabola respectively up to 700° C., but the differences in either case far exceed the possible errors of observation (fig. 3). In order to exhibit any peculiar points on a satisfactory scale in either case, difference-curves were constructed. For copper-nickel, differences from a straight line were plotted from the equation

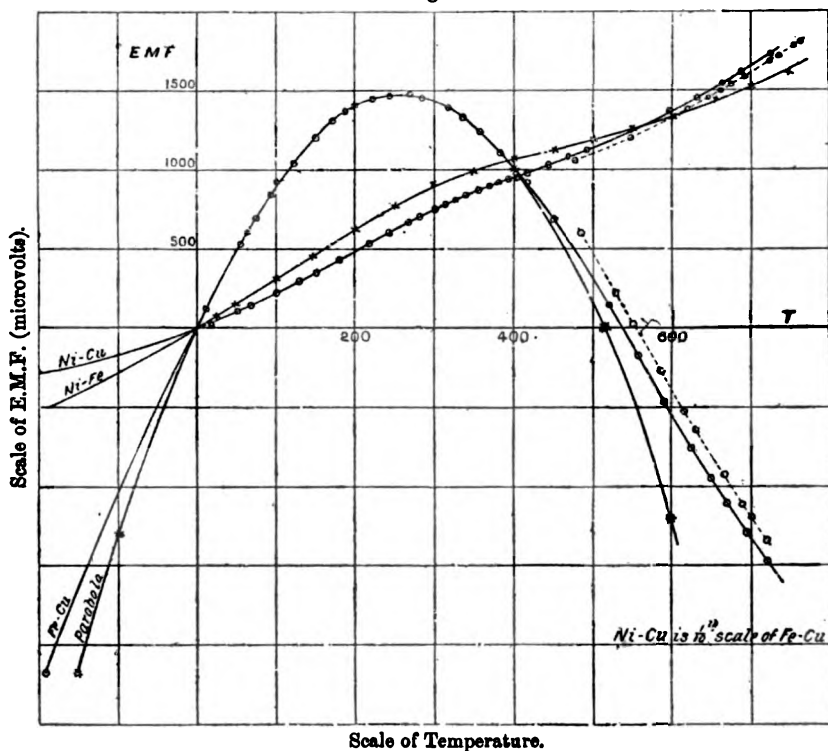
$$\text{Difference} = E_{\text{observed}} - 22t.$$

Values of  $D$  (difference) thus obtained were plotted against temperature (Curve  $D$  (Ni), fig. 4). In a similar way for the iron-copper couple a parabola

$$E_s^t = 11.228t - 0.021924t^2,$$

passing through the ice, aniline, and sulphur points, was calculated, and differences from this parabola were plotted.

Fig. 3.



This gives Curve  $D$  (Fe), fig. 4. In this case differences are much smaller than in the case of the nickel. The parabola itself is shown in fig. 3.

From these differences it is seen that maximum variations occur in the case of Cu-Fe, ( $\alpha$ ) at  $70^\circ$ , when the thermoelectric E.M.F. is less than the corresponding parabolic



Fig. 4.—Difference Curves.

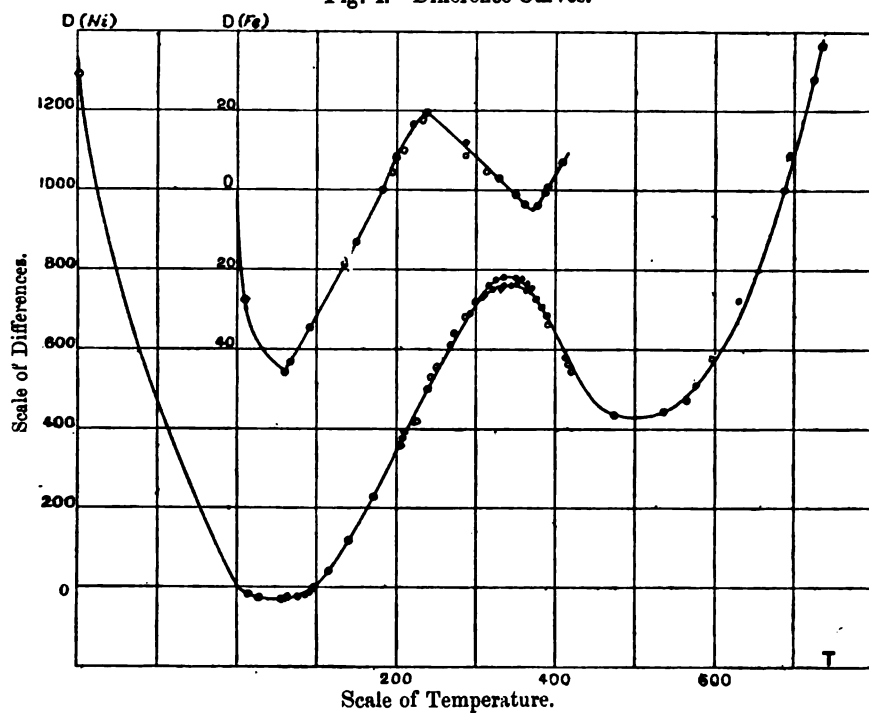
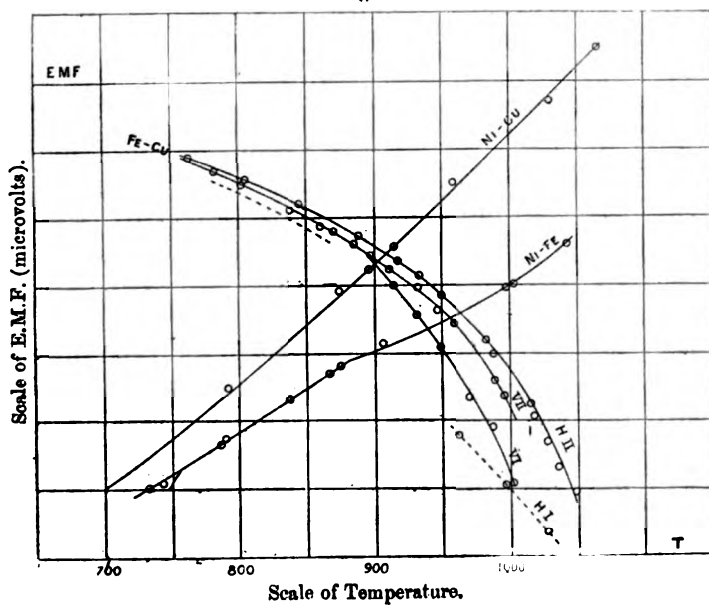


Fig. 5.



ordinate by 45 microvolts; (*b*) at  $230^{\circ}$ , when the thermoelectric E.M.F. is greater than the corresponding parabolic ordinate by 20 microvolts; (*c*) at  $370^{\circ}$ , when the thermoelectric E.M.F. is again less than the corresponding parabolic ordinate by 5 microvolts. Between  $0^{\circ}$  and  $200^{\circ}$ , and between  $400^{\circ}$  and  $750^{\circ}$  there is a gradual divergence from parabolic form more strongly marked on the hot side (the reverse of Tait's observation).

The temperature of inversion, cold junction at  $0^{\circ}$ , is found to be  $536^{\circ}$  C., and is given by the intercept on the axis of temperature, between  $0^{\circ}$  and the point of section by the curve of thermoelectric power (fig. 6, p. 69).

The neutral point is at  $262^{\circ}$  C.

Above  $700^{\circ}$ , Cu-Fe E.M.F. increases almost as a linear function of the temperature till  $900^{\circ}$  is reached, when a rapid increase in the E.M.F. is noticed, with no indication of a second neutral point (fig. 5).

In the case of Cu-Ni, maximum variations occur at about  $70^{\circ}$  C. and  $340^{\circ}$  C. The divergence at  $340^{\circ}$  is very marked, and after  $500^{\circ}$  C. increases rapidly. There appears to be a small hysteresis effect at the maximum. The temperature of inversion, if there be one, does not occur within the limits of the experiment, and there is no neutral point. Above  $700^{\circ}$ , the Cu-Ni curve (fig. 5) remains almost linear up to  $1050^{\circ}$ , the limit of the experiments, while the slope of the curve is practically unchanged.

The E.M.F. curve for Ni-Fe couple (fig. 3) up to  $700^{\circ}$  C. was obtained by adding the ordinates of the copper-nickel and copper-iron curves corresponding to definite temperatures. It has no neutral point above  $0^{\circ}$ , though at the temperature of liquid air there is an indication of one. The fact that no neutral point occurs in the iron-nickel "line" is also evident from the fact that copper-nickel and copper-iron thermoelectric-power curves, when plotted on the same scale, do not intersect.

The E.M.F. curve is a nearly linear function of the temperature up to about  $900^{\circ}$ , when a decrease in the E.M.F. is noticed (fig. 5). Above  $700^{\circ}$  the curve was obtained by direct observation of the E.M.F. of a fresh nickel-iron couple, the copper being omitted in order to avoid the

uncertainty due to its evaporation, which became quite appreciable at  $900^{\circ}$  C. The junction of iron and nickel was made by fusing the wires in the electric arc.

The dotted parts of the nickel and iron "lines" (fig. 3) were obtained when the couples were known to be affected by oxidation, *i. e.* when the vacuum was known to be faulty. The shift only occurred at the higher temperatures. The E.M.F., when determined on the same "oxidized" couple for lower temperatures (such as  $200^{\circ}$ ), coincided with the original values. Any error in measuring temperature or E.M.F. would be constant for the copper-nickel and copper-iron "lines." The observed facts, however, show that the effect is not the same in the two cases. The vertical displacement of the nickel curve is about 425 microvolts, while at the same temperature that of the iron curve is about 120 microvolts, the horizontal shift in the first case being  $14^{\circ}$ , and in the second case  $18^{\circ}$ , in the same direction.

The effect for Cu-Fe is as if an applied E.M.F. were acting so as to produce a current in the same direction as that due to the junction. Thus the fact that the effect is an increase of ordinate above  $500^{\circ}$ , and a decrease of ordinate below  $500^{\circ}$  (in the case of Fe-Cu) is accounted for. For Cu-Ni there is always a decrease, such as might be due to an E.M.F. giving a current in the opposite direction to that due to the junction. Moreover, the two dotted bits are not absolutely parallel to the original curves, making it still more probable that the explanation of the shift is to be found in the fact that chemical action took place and altered the E.M.F.'s.

When the couples were heated in hydrogen, so as to preclude the possibility of oxidation, those points taken below  $895^{\circ}$  C. lay on the main curve, which bears out the idea that the shift in question is due to oxidation.

Above  $895^{\circ}$  other effects were observed when the couples were heated in hydrogen, which were more systematically investigated (see below).

In carbon, observations taken up to  $700^{\circ}$  agreed with the hydrogen and vacuum results. Above this temperature, carbides of iron are probably formed which give rise to the inconsistency in the results, which has already been

remarked on. It may be mentioned that these observations gave values of E.M.F. which were considerably greater than those in hydrogen.

It is evident that thermoelectric couples of copper-iron and copper-nickel packed in carbon will give consistent readings of E.M.F. up to  $700^{\circ}$  or  $800^{\circ}$ , but that above this temperature the method fails.

Under every condition tried, copper, nickel, and iron wires were always extremely brittle after heating above  $700^{\circ}$ . After heating in hydrogen they were invariably quite bright, notably the copper. This last metal volatilized considerably above  $900^{\circ}$ .

The curves of thermoelectric power  $\frac{dE}{dt}$ , shown in fig. 6, were obtained by drawing tangents to the E.M.F. curves (figs. 3 and 5). A considerable range

$$\left( \begin{array}{c} \text{from } -200^{\circ} \text{ to } +100^{\circ} \\ \text{and from } +100^{\circ} \text{ to } +400^{\circ} \end{array} \right)$$

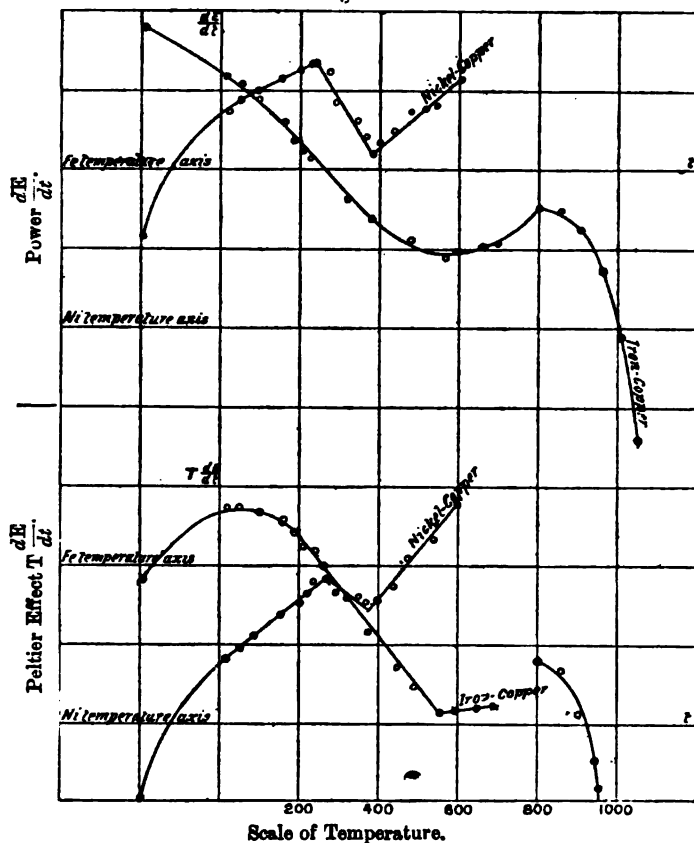
of the copper-iron curve can be represented by straight lines. Between  $+400^{\circ}$  and  $+800^{\circ}$ , however, the curve appears to be parabolic, and cannot be built up of bits of straight lines.

Above  $800^{\circ}$   $\frac{dE}{dt}$  increases rapidly, being nearly linear between  $900^{\circ}$  and  $1050^{\circ}$ . The Cu-Ni power curve can be represented by bits of straight lines. Changes in slope occur at  $240^{\circ}$  and  $380^{\circ}$ .

The Peltier coefficients  $T \frac{dE}{dt}$ , obtained by multiplying the thermoelectric power by the corresponding absolute temperature, are given in the same figure (fig. 6). The curve for iron-copper is approximately parabolic between  $-200^{\circ}$  and  $+300^{\circ}$ . After that it can be made up of straight lines. The break just below  $800^{\circ}$  is due to the fact that the E.M.F. curve for results above  $800^{\circ}$  did not quite join, but was approximately parallel to that for lower temperatures. For Cu-Ni the Peltier coefficient-variation can be built up of bits of parabolas, if the power-curve is strictly linear; but uncertainty in the values obtained by differentiating an E.M.F. curve makes it better to show the Peltier coefficient-variation as bits of straight lines.

Changes in sign of the Thomson coefficient, or specific heat of electricity, are indicated by these changes in slope of the Peltier coefficient, and the former are remarked on by

Fig. 6.



Tait, and he gives the temperatures at which they occur as just above  $200^\circ$ , and again just below  $300^\circ$ . It is also evident that the E.M.F. curve for Cu-Ni can be represented very well by bits of parabolas over the whole range.

*Changes in E.M.F. on heating above  $900^\circ$ .*

It was noticed that changes in the value of the E.M.F. for any particular temperature occurred on *continued* heating,

and in order to investigate these changes observations were made with the Fe-Cu couple under the following four conditions :—

- (i.) New couple in air-vacuum.
- (ii.) Same couple after continued heating in air-vacuum.
- (iii.) New couple in hydrogen at about 860 mm. pressure.
- (iv.) Same couple after continued heating in hydrogen.

(i.) On heating a new couple rapidly to the highest temperature required, and then taking observations throughout the range as quickly as is consistent with accuracy, Curve V I. was obtained (fig. 5).

The E.M.F. increases almost as a linear function of  $t$  up to about  $895^{\circ}\text{C.}$ , when an abrupt change of slope occurs and the E.M.F. increases more rapidly up to the limit of the experiments.

(ii.) Using the same couple after 10 or 15 hours' heating, the abrupt change of slope previously noticed no longer occurs, but as is seen by V II., the curve is continuous over the whole range so that above  $895^{\circ}$  the curve consists of two branches, the lower one obtained with a once-heated couple and the upper one with a couple that had undergone more prolonged heating, while below  $895^{\circ}$  the curve is common to the two branches, and appears to be independent of the length of time the couple has been heated. Measurements were then made with continuously rising and continuously falling temperatures to find if hysteresis occurred above  $890^{\circ}$ . Evidence was obtained of small effects of this nature, slightly greater values of E.M.F. being obtained with falling temperature, though any exact estimation of the phenomenon was made somewhat difficult by the change which was going on in the value of the E.M.F. owing to continued heating.

"Lag" errors due to a temperature which was changing too rapidly would not account for these effects, for such errors would affect the result in the opposite direction—for instance, with a too rapidly falling temperature the curve would be shifted upwards owing to "lag" in the recording of the temperature.

The variation of E.M.F. above  $900^{\circ}$  is about 20 microvolts per degree for the freshly heated couple. Probably the

effects of continuous heating are going on the whole time in Curve V I.: hence the rapid, though continuous change of slope. At  $895^{\circ}$  a change, most likely chemical, occurs in the Fe, and below this temperature the couple is in a new state, and secular changes go on more slowly, if at all.

After these experiments the copper was exceedingly bright while the iron was covered with a black deposit.

(iii.) When a new couple is heated in hydrogen, Curve H I. is first obtained, no change of slope being noticeable and the values for the E.M.F. being greater than those obtained in a vacuum. This curve therefore approximates more nearly at  $700^{\circ}$  to the one obtained at lower temperatures, than does V I., the lowering of the curve under the influence of hydrogen being consistent with previous observations on the effect of this gas.

(iv.) After continued heating in hydrogen, just as in Curve V II., the values of the E.M.F. become less, and finally the curve representing them lies slightly above the values obtained *in vacuo* (Curve H II.). H II. is nearly, but not quite, parallel with V II. The wires at the end of the experiments were both perfectly clean although the iron had lost its polish. The copper was exceedingly bright.

In the case of iron heated in hydrogen, possibly a gradual reduction of impurities in the substance of the iron accounts for the change in the E.M.F. on continued heating.

[There is no break or change of slope in the thermoelectric curves for Cu-Fe at  $800^{\circ}$ , the temperature at which the resistance of Fe alters.]

In order to eliminate any possible effect of the copper, a Ni-Fe couple was used. The E.M.F. was affected by continued heating in hydrogen, in just the same way as when copper was present. Evidently the effect is due to physical or chemical changes or both going on in the iron, and the change of slope at  $895^{\circ}$  is not connected with a decomposition of copper oxide at this temperature, as was at one time thought possible.

Only the means of the observations of E.M.F. at the temperatures of steam, aniline, sulphur vapour, and liquid air are given in the table below.

The observations at other parts of the curves were much

more numerous than those shown by circles in the figures, but they could not be satisfactorily represented by means of tables or empirical formulæ, on account of the singularities presented in the variations of E.M.F. The E.M.F. at any temperature can be very accurately deduced from the difference curves, *e. g.* for copper-iron at  $250^{\circ}$

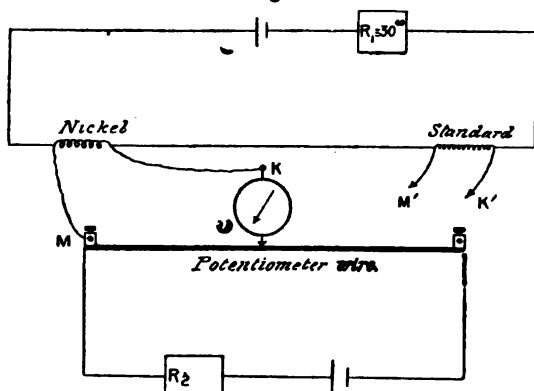
the parabolic formula gives . . . .	+ 1452.1 microvolts.
the reading of Curve D (Fe) gives . .	+ 17.5        „
Hence Total E.M.F. is . . . . .	<u>+ 1469.6</u> „

## SECTION II.

### *Resistance Experiments.*

A potentiometer method was used and the general arrangement of the apparatus is shown in fig. 7.

Fig. 7.



The wire the resistance of which was to be measured was wound into a spiral, and the main current leads and potential leads of No. 28 B.W.G. copper were silver-soldered to the ends of the spiral; the other extremities of these four leads being soldered to four No. 18 copper leads which projected through the cork of the porcelain tube. The thin copper was used in order to minimise conduction of heat from the spiral. The standard coil for comparison was of manganin and, with its potential leads, was immersed in paraffin oil. It was not found necessary to apply any correction for temperature changes in the standard.

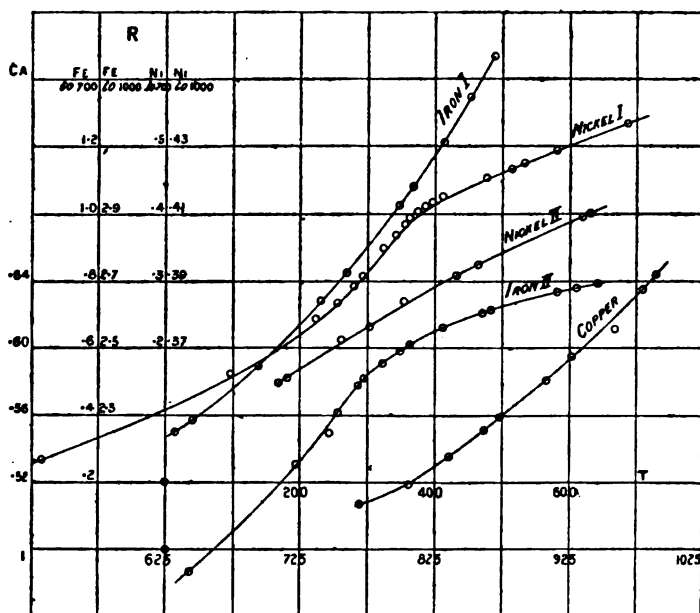


The porcelain tube containing the spiral was placed in the heater as before, with a pyrometer. Care was taken that the temperature was steady before making an observation of resistance, and in every case a reading of the standard resistance was taken before and after each reading of the resistance (Ni or Fe) required.

### Discussion of Results.

The resistance of nickel increases with temperature almost parabolically up to  $370^{\circ}$ , when a change of slope occurs, and the resistance increases much less rapidly and almost as a linear function of the temperature up to  $1050^{\circ}$  (fig. 8).

Fig. 8.



A parabola which fitted the resistance observations very well up to  $350^{\circ}$  C. was calculated passing through  $\pm 100^{\circ}$  and  $+300^{\circ}$ , and was plotted from the equation

$$R_{Ni} = .10288 + .00048t - .0000007126t^2.$$

The change of slope in the nickel resistance-curve is not sudden but extends over  $10^{\circ}$  or  $15^{\circ}$ .

In the case of iron, the resistance-curve does not change its parabolic form till nearly  $800^{\circ}$ , when it becomes linear and remains so within the limits of the experiments.

The parabola

$$R_{Fe} = .3318 + .001230t + .000002209t^2$$

fitted the iron resistance-curve up to  $500^{\circ}$ .

The shape of the nickel and iron resistance-curves are strikingly alike at the temperature of the change in each.

There was very little oxidation in these high-temperature experiments; in most cases the copper leads at their junction with the spirals appearing perfectly bright. A reddish deposit (apparently of metallic copper) was usually seen on the spiral and mica disks.

A further series of measurements was made in hydrogen. No change whatever in the temperature at which the change of slope for iron occurred was produced by this, although the two curves were not absolutely coincident.

The change of resistance for copper was determined between  $750^{\circ}$  and  $1000^{\circ}$ . The copper wire (No. 28 B.W.G.) was wound on a mica frame and was heated in hydrogen. It is known that up to  $500^{\circ}$  or  $600^{\circ}$  the resistance of copper changes like platinum. The present experiments show that above that temperature a point of inflexion occurs, and the resistance-curve becomes convex towards the temperature axis.

Above  $800^{\circ}$  the curve is nearly linear, with another less clearly defined change of slope just below  $1000^{\circ}$ .

The main object of the present research was originally to correlate the peculiar thermoelectric points with the changes of slope on the resistance-curves.

The result from this point of view is that the thermoelectric change in nickel-copper coincides approximately with the resistance change, but that no thermoelectric peculiarity exists for iron-copper at the temperature of the Fe resistance change. As is shown by the Peltier coefficients, a marked change occurs at about  $500^{\circ}$  in the case of Fe-Cu. This is approximately the temperature at which a flexure occurs in the copper resistance-curve.

*Numerical Results.*

E.M.F. in microvolts.	Temperature (Air-Therm.).	Note.
<i>Copper-Nickel.</i>		
-2907	-191.2	Liquid air.
2233	99.8	Steam.
10335	445.5	Sulphur vapour.
4321	182.5	Aniline vapour.
<i>Copper-Iron.</i>		
-2195	-191.2	Liquid air.
1334	182.5	Aniline.
870	99.9	Steam.
684	445.5	Sulphur vapour.
98	11.2	
<i>Iron-Nickel.</i>		
-5111	-191.2	Liquid air.
11807	500	
3130	100	
6160	200	

*Peltier Coefficients.*

$T \cdot \frac{dE}{dt}$ .	Temperature.	Note.
<i>Copper-Iron.</i>		
+1156	-191.2	Liquid air.
<i>Copper-Nickel.</i>		
-7697	-191.2	Liquid air.

*A Comparison with Fleming's Results for Iron, Copper, and Nickel-Copper.*

	Present Experiments.	Fleming and Dewar's.
	E.M.F. in microvolts.	E.M.F. in microvolts.
<i>Copper-Nickel.</i>		
Liquid air.	-2007	-2380
100° C	2233	2205
<i>Copper-Iron.</i>		
Liquid air.	-2191	-2560
100° C.	870	1138
<i>Nickel Iron.</i>		
Liquid air.	-5111	-4969

It is perhaps worth noticing that if the dotted part of the Fe-Cu curve (fig. 5) (which is marked HI and represents the first few points obtained by heating a fresh couple in hydrogen) be produced, it cuts the upper and "constant" portion of the curve at a temperature just below 800°, the temperature of the resistance-changes in iron.

In conclusion I wish to express my best thanks to Professor Callendar, F.R.S., for constant help and advice during this research, which was undertaken at his suggestion.

My thanks are also due to Mr. G. M. Gibbins, of University College, for help during the first part of the thermoelectric measurements.

#### DISCUSSION.

Mr. A. CAMPBELL said that with purer iron the change in thermoelectric properties might correspond with the change in resistance. Dr. Knott had performed experiments on nickel in 1886 and got results similar to those of the author. Mr. Campbell said that he had himself made experiments upon two samples of nickel differing widely in resistivity, and although their temperature coefficients were also different, the change in slope of the curve connecting resistance

and temperature occurred at practically the same temperature in both specimens. Their thermoelectric powers, however, were almost identical up to  $300^{\circ}$ , but above they differed slightly.

Dr. D. K. MORRIS pointed out that the thermoelectric force, the resistance, and the magnetic properties should be observed at the same time. In taking a thermoelectromotive force there must be a temperature gradient, and in the interesting parts of the curves differences of magnetic properties may arise and produce discrepancies. He drew attention to the caution which must be exercised in differentiating by drawing tangents except when the curves are smooth. Dr. Morris said the connexion between resistance and magnetic qualities was interesting. The temperature coefficient of resistance of a magnetic body rises with temperature so long as the body is magnetic, but decreases when the body becomes non-magnetic; and this connexion holds even when a substance (as manganese steel) exists at the *same temperatures* in both states. He asked for information on the subject.

Prof. H. L. CALLENDAR said he had followed the research with interest, and referred to the experimental difficulties, especially at high temperatures. He should like to have said something in reply to Dr. Morris, but he was afraid the subject was a large one, and might well be discussed at some future meeting. There were several points to clear up, and the fact that the curves described cannot be represented by straight lines or parabolas showed that the subject was beyond the range of a simple theory.

Prof. THOMPSON suggested that it might be well to re-examine more carefully some of the curves which are accepted as straight lines, and on which there is no complication due to magnetic properties. He hoped the author and others would continue working at this subject.

Mr. E. P. HARRISON, in reply to Dr. Morris, said he thought the number and accuracy of his observations justified him in drawing tangents to form his power and Peltier effect curves.

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III. *On Asymmetry of the Zeeman Effect.* By GEORGE W. WALKER, M.A., A.R.C.Sc., Fellow of Trinity College, Cambridge\*.

IN his valuable papers on the Zeeman Phenomenon, Professor W. Voigt† predicted an asymmetry of the normal triplet in the sense that the new component lying towards the violet end should be at a greater distance from the central component than the new component lying towards the red end of the spectrum. Professor Zeeman has verified this and is endeavouring to measure the amount, which is excessively small.

Professor Voigt finds that

$$\delta = -\xi \pm \sqrt{c^2 R^2 + \xi^2},$$

where  $\tau_0$  and  $\tau$  are the undisturbed and disturbed periods

$$S = \frac{\tau}{2\pi}, \quad S_0 = \frac{\tau_0}{2\pi}, \quad \delta = S - S_0,$$

$$\xi = \epsilon_1 S_0;$$

$R$  = strength of the magnetic field.

The quantities  $\epsilon_1$  and  $c$  are constants depending on the system which produces the fundamental line.  $\xi$  is supposed very small, and upon it the asymmetry depends; for if  $\xi=0$  we get

$$\delta = \pm cR,$$

which represents the ordinary Zeeman effect. If  $\xi$  is retained we see that the asymmetry will be most marked in a weak magnetic field.

I find that asymmetry may be accounted for as a second order term arising from the magnetic field, and will now obtain the result.

Let us take as our representative molecule producing radiation, a system consisting of two atoms equally and

\* Read October 25, 1901.

† *Annalen der Physik und Chemie*, lxvii. 1899, p. 345; *ibid.* i. 1900, p. 376.

oppositely charged. Let the charge be  $e$  and the effective masses  $m_1$  and  $m_2$  respectively. In order to avoid difficulties about the law of force between the two atoms we shall consider the motion as a disturbed circular orbit, so that we may write the equations of motion as

$$\begin{aligned} m_1 \ddot{x}_1 + a^2(x_1 - x_2) &= eH \dot{y}_1, & m_2 \ddot{x}_2 - a^2(x_1 - x_2) &= -eH \dot{y}_2, \\ m_1 \ddot{y}_1 + a^2(y_1 - y_2) &= -eH \dot{x}_1, & m_2 \ddot{y}_2 - a^2(y_1 - y_2) &= +eH \dot{x}_2, \\ m_1 \ddot{z}_1 + a^2(z_1 - z_2) &= 0, & m_2 \ddot{z}_2 - a^2(z_1 - z_2) &= 0, \end{aligned}$$

where  $x_1, y_1, z_1, x_2, y_2, z_2$  are the coordinates of the centres of the two atoms and  $H$  is the strength of magnetic field supposed uniform and parallel to the  $z$  axis.

In general  $a$  in these equations may differ slightly from the undisturbed value, but for the present purpose this does not matter.

As first integrals of the equations we get

$$\begin{aligned} m_1 \dot{x}_1 + m_2 \dot{x}_2 &= (m_1 + m_2)u + eH(y_1 - y_2), \\ m_1 \dot{y}_1 + m_2 \dot{y}_2 &= (m_1 + m_2)v - eH(x_1 - x_2), \\ m_1 \dot{z}_1 + m_2 \dot{z}_2 &= (m_1 + m_2)w, \end{aligned}$$

where  $u, v, w$  are constants of integration.

Using these equations and putting

$$p_0^2 = a^2 \left( \frac{1}{m_1} + \frac{1}{m_2} \right),$$

$$x_1 - x_2 = \xi, \quad y_1 - y_2 = \eta, \quad z_1 - z_2 = \zeta,$$

we get

$$\begin{aligned} \ddot{\xi} + p_0^2 \xi + \frac{e^2 H^2}{m_1 m_2} \xi &= \frac{eH(m_2 - m_1)}{m_1 m_2} \dot{\eta} + \frac{eH(m_1 + m_2)}{m_1 m_2} v, \\ \ddot{\eta} + p_0^2 \eta + \frac{e^2 H^2}{m_1 m_2} \eta &= -\frac{eH(m_2 - m_1)}{m_1 m_2} \dot{\xi} - \frac{eH(m_1 + m_2)}{m_1 m_2} u, \\ \ddot{\zeta} + p_0^2 \zeta &= 0. \end{aligned}$$

The terms in  $u$  and  $v$  have no influence on the periodic parts of  $\xi$  and  $\eta$ . Hence putting  $\xi, \eta, \zeta$  proportional to  $e^{ipt}$ , we get for the  $\xi$  vibration

$$p = p_0,$$

and for the  $\xi$  and  $\eta$  vibrations the roots of  $p$  given by

$$p^2 - p_0^2 - \frac{e^2 H^2}{m_1 m_2} = \pm \frac{e H (m_2 - m_1)}{m_1 m_2} p;$$

and hence

$$p = \pm \frac{1}{2} \frac{e H (m_1 - m_2)}{m_1 m_2} + p_0 \sqrt{1 + \frac{e^2 H^2 (m_1 + m_2)^2}{4 p_0^2 m_1^2 m_2^2}}.$$

Neglecting squares of

$$\frac{e^2 H^2 (m_1 + m_2)^2}{4 p_0^2 m_1^2 m_2^2}$$

we get

$$p = p_0 \pm \frac{1}{2} \frac{e H (m_1 - m_2)}{m_1 m_2} + \frac{1}{8} \frac{e^2 H^2 (m_1 + m_2)^2}{p_0 m_1^2 m_2^2}.$$

Putting

$$p = \frac{1}{S}, \quad p_0 = \frac{1}{S_0}, \quad \delta = S - S_0,$$

we get

$$\delta = \pm \frac{1}{2} \frac{e H (m_2 - m_1)}{m_1 m_2} S_0^2 - \frac{1}{8} \frac{e^2 H^2 (m_1 + m_2)^2}{m_1^2 m_2^2} S_0^3.$$

The new lines looking at right angles to the field are therefore:—

The central line  $S = S_0$  polarized perpendicular to the direction of the lines of force, and the lateral components

$$\delta + S_0 = S_0 \pm \frac{1}{2} \frac{e H (m_2 - m_1)}{m_1 m_2} S_0^2 - \frac{1}{8} \frac{e^2 H^2 (m_1 + m_2)^2}{m_1^2 m_2^2} S_0^3. \quad (A)$$

polarized perpendicularly to the central line.

The first term represents the ordinary Zeeman effect. For comparison I rewrite Voigt's formula

$$\delta = -\xi \pm \sqrt{c^2 R^2 + \xi^2},$$

or approximately

$$\delta = \pm cR - \xi \pm \frac{1}{2} \frac{\xi^2}{cR} \dots$$

The asymmetry is therefore in the same sense in the two theories, viz., the lateral component towards the violet having the greater displacement. They differ, however, in one important respect. On the present theory the asymmetry is greater the greater the strength of the magnetic



field, whereas on Voigt's theory it is more marked the smaller the field.

The term

$$\pm \frac{1}{2} \frac{eH(m_2 - m_1)}{m_1 m_2} \mathfrak{S}_0,$$

in this theory is of course the same as  $\pm cR$  in Voigt's theory.

Let us next compare the effect in different parts of the spectrum.

On Voigt's theory the difference of displacement of the two components is

$$2\xi \quad \text{or} \quad 2\epsilon_1 \mathfrak{S}_0,$$

and the fraction of the separation is

$$\frac{2\xi}{2cR} \quad \text{or} \quad \frac{\epsilon_1 \mathfrak{S}_0}{cR}: \quad \text{that is} \quad \propto \frac{1}{\mathfrak{S}_0 \times H}.$$

On the present view the difference of displacement is

$$\frac{1}{4} \frac{e^2 H (m_1 + m_2)^2}{m_1^2 m_2^2} \mathfrak{S}_0^2,$$

and the fraction of the separation is

$$\frac{1}{4} \frac{eH(m_1 + m_2)^2}{m_1 m_2 (m_1 - m_2)} \mathfrak{S}_0.$$

On both views, then, the actual difference of displacement is greater, other things being equal, at the red end. But the fraction which the asymmetry is of the separation would be greater at the violet end of the spectrum on Voigt's theory, and greater at the red end on the present theory. This has an important bearing on the experimental detection of the effect.

We may further consider the probable numerical values.

The quantity  $\epsilon_1$  is connected with the molecule in such a way that the dielectric constant

$$K = 1 + \Sigma \epsilon_1,$$

the summation referring to all the molecules:  $\epsilon_1$  is thus a quantity of order about  $10^{-25}$ , and if  $\mathfrak{S}_0 = 4 \times 10^{-16}$ ,

$$\xi \text{ is of order } 4 \times 10^{-41}.$$

If, as a variety of experimental work indicates,  $m_2$  is very small compared with  $m_1$ , the formula (A) becomes

$$\delta = \mp \frac{1}{2} \frac{eH}{m_2} \mathfrak{S}_0^2 - \frac{1}{8} \frac{e^2 H^2}{m_2^2} \mathfrak{S}_0^3.$$

For a field of  $10^4$  C.G.S. units we may take  $\frac{eH}{m_2}$  about  $10^{11}$ ;

therefore  $\frac{1}{2} \frac{eH}{m_2} \mathfrak{S}_0^2$  is about  $8 \times 10^{-21}$ ,

and  $\frac{1}{8} \frac{e^2 H^2}{m_2^2} \mathfrak{S}_0^3$  is about  $8 \times 10^{-26}$ .

Thus  $\xi$  appears to be very small compared with

$$\frac{1}{8} \frac{e^2 H^2}{m_2^2} \mathfrak{S}_0^3,$$

and the latter term might just come within measurable amount by increasing the field.

One more point in connexion with the proposed view may be noted, which is that it provides an explanation of why a line may not be resolvable. If  $m_1 = m_2$  there would be no doubling of the line, but only a small shift towards the violet. In this case the system is dynamically symmetrical.

It is almost unnecessary to remark that the simple system selected for discussion is merely illustrative of the characteristic features of the problem.

#### IV. *A Voltameter for Small Currents.*

*By R. A. LEHFELDT.*

IN the course of some experiments with mercury voltmeters I had a conversation with Mr. E. C. C. Baly, during which the suggestion of a remarkably simple form of instrument arose. This I have realized in practice, as follows:—

A glass tube of from 0.5 to 1.5 mm. bore is provided with a pair of platinum electrodes, sealed in near the ends; the

\* Read November 8, 1901.

ends are then drawn out to a small diameter. The tube so prepared is filled—by means of the water-pump—with mercury throughout, except for one drop of mercurous-nitrate solution in the middle of its length; the ends of the tube are then sealed off. The tube is placed vertically, and the upper portion of mercury made the anode, the lower the cathode. The drop of solution creeps up the tube at a rate proportional to the current flowing, the movement being measured by any convenient scale, preferably one etched on the glass, with or without a micrometer.

For the successful construction of the apparatus the following points should be attended to :—The parts of the tube where the electrodes are sealed-in should not be widened, else difficulty in filling is likely to ensue. The filling can be done by placing the tube—askant—with one point dipping under mercury, in a dish. The mercury is covered by solution : when enough has been drawn in by the pump to form one electrode, the point is lifted momentarily so as to allow solution to flow in instead ; then depressed, when more mercury enters, to form the other electrode. The filling is regulated most conveniently by a tap sealed on to the upper end of the tube, which is subsequently detached. The solution is made by weighing out about 26·3 milligrams of mercurous nitrate per c.c. of water (*i. e.* decinormal), and adding enough nitric acid to dissolve the basic salt that forms. The current-density may be anything up to 10 or 15 milliamperes per sq. cm. ; more than that causes polarization. Hence a tube of 2 sq. mm. cross-section (ordinary Sprengel-pump tubing) will take 0·3 milliampere.

The electrochemical equivalent of mercurous mercury is 7·470 grams per ampere per hour, or 0·5509 c.c. Hence with a current-density of 0·010 ampere/sq. cm., the rate of movement would be 0·005509 cm. per hour, or about 1 mm. a day. The meter is therefore eminently adapted to measure long-continued currents of very small magnitude. Moreover, with proper precautions it may be shunted, as, apart from temperature changes, the resistance keeps steady.

The following is a record of such an instrument :—

G 2

Cross-section of tube 0·624 mm.: length of thread of solution about 6 mm. Micrometer used, 1 scale-division = 0·0785 mm.

	Time.		Micrometer.	
	h	m		
Oct. 18.	11	10	40·0	Started current of 1/12000 amp.
	12	15	41·0	
	13	15	42·0	Stopped.
Oct. 21.				Reset micrometer.
	11	50	40·0	Started current of 1/12000 amp.
	15	40	43·7	
Oct. 22.	9	50	60·5	

Calculated rate of movement 1 micrometer-division in 1·067 hours; observed rate 1·073. The small discrepancy is no doubt due to errors of experiment, and could be diminished by greater care in calibration, measurement of current, and of distance moved.

#### DISCUSSION.

Mr. BLAKESLEY pointed out that the presence of air in the tube would render the readings inaccurate, and asked if it was necessary to apply any temperature correction.

Dr. LEHFELDT said that it was quite easy to seal the tube without admitting air, and the temperature correction was negligible.

V. *Note on a Paper by Prof. Fleming, F.R.S., and Mr. Ashton, entitled "On a Model which Imitates the Behaviour of Dielectrics."* By JOHN BUCHANAN, D.Sc. (Lond.)\*.

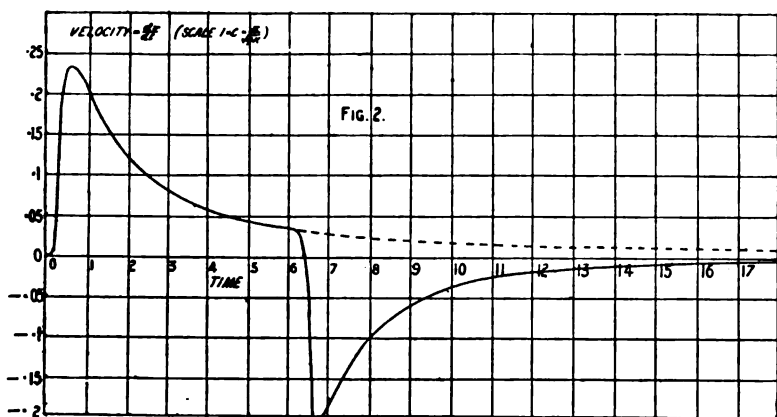
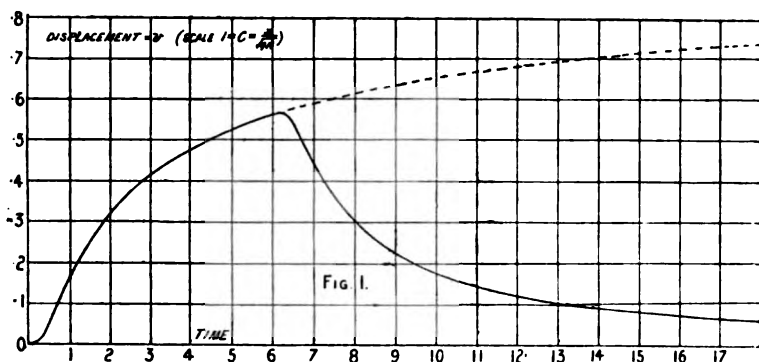
UNDER the above title there has appeared in the Phil. Mag. for August 1901 a description of a very ingenious model invented by the authors of the paper. The diagrams, obtained by help of the model, which illustrate the paper are exceedingly interesting and suggestive.

There are some points in the theory of the action of the model, and of the behaviour of the dielectric in a condenser, which may be deemed worth attention.

1. The action of the model clearly depends on the viscosity

\* Read November 8, 1901.

of a liquid. The diagrams show by their form the very interesting fact that the motion of the pencil which traced them approximated closely to what may be expressed by the term "motion of a viscous fluid by diffusion"\*.



In other words, the displacement curves obtained from the model, and their derived velocity curves, are of the same form as the graphs of certain solutions of Fourier's well-known equation

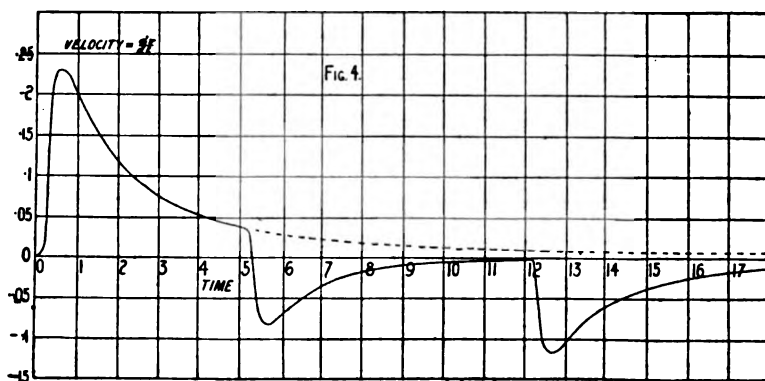
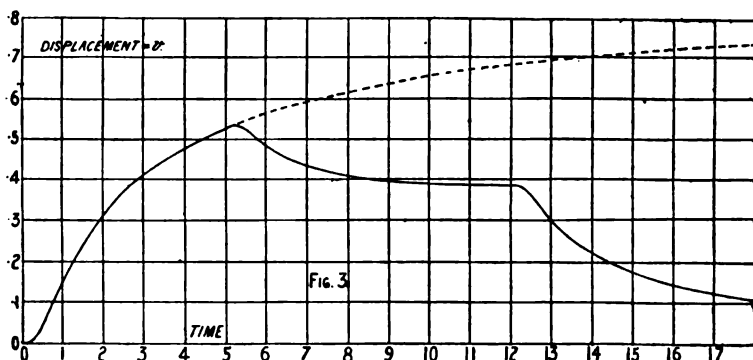
$$\frac{dv}{dt} = K \frac{d^2v}{dx^2}. \quad \dots \dots \dots (1)$$

For comparison with figs. I. & III. (Pl. V.) respectively, of Prof. Fleming and Mr. Ashton's paper, I give here figs. 1 and 2, which are the respective graphs of equations (2)

\* Cf. Lord Kelvin's Math. and Phys. Papers, vol. iii. art. xcvi. p. 433.

and (3) below. In these solutions of (1)  $v$  denotes the displacement,  $t$  the time,  $x$  the distance from the origin at which exists the motion under consideration, and  $K$  denotes the "diffusivity."

Without the guidance afforded by some such theory as is here given, it would be quite impossible to discover from experiment such a law of displacement as is expressed by (2) for instance, or of velocity as expressed by (3). Thus, the



right-hand member of (2) expresses that when  $t=0$  a sudden displacement  $C$  (= "charge") is impressed on the model at the point  $x=0$ . This displacement is maintained until a time  $t=T$  has elapsed, when release (= "discharge") is allowed to take place.

As an example of a more complex set of operations, for comparison with fig. v, Pl. V. *loc. cit.*, I give here figs. 3 & 4.

The former is the graph of (4) below, the latter is the derived velocity-curve.

We can from these examples see how, by solutions of (1), we can express the effect of any given set of conditions as regards "charge" or "discharge."

The solutions of (1) referred to above are :—

$$v = C \left( 1 - \frac{2}{\sqrt{\pi}} \int_0^{\frac{x}{\sqrt{4Kt}}} dz e^{-z^2} \right) - C \left( 1 - \frac{2}{\sqrt{\pi}} \int_0^{\frac{x}{\sqrt{4K(t-T)}}} dz e^{-z^2} \right), \quad (2)$$

$$\frac{dv}{dt} = C \frac{x}{\sqrt{4\pi K}} \left( \frac{e^{-\frac{x^2}{4Kt}}}{t^{\frac{3}{2}}} - \frac{e^{-\frac{x^2}{4K(t-T)}}}{(t-T)^{\frac{3}{2}}} \right). \quad (3)$$

Also,

$$v = C \left( 1 - \frac{2}{\sqrt{\pi}} \int_0^{\frac{x}{\sqrt{4Kt}}} dz e^{-z^2} \right) - \frac{C}{2} \left( 1 - \frac{2}{\sqrt{\pi}} \int_0^{\frac{x}{\sqrt{4K(t-T)}}} dz e^{-z^2} \right) - \frac{C}{2} \left( 1 - \frac{2}{\sqrt{\pi}} \int_0^{\frac{x}{\sqrt{4K(t-T)}}} dz e^{-z^2} \right). \quad (4)$$

2. The reasons why the model gives curves of the same form as the curves of "charge" and "discharge" of a condenser appear fairly obvious.

Lord Kelvin showed long ago in his paper "On the Theory of the Electric Telegraph"\*, that the potential and the current at any point in the wire of a cable can be expressed by appropriate solutions of (1) above. In precisely the same manner, by use of solutions of (1) we can treat the question of the diffusion of electricity into or out of the dielectric of a condenser. That such a dielectric has usually an enormous resistance per centim. compared with a centim. length of the wire of a cable, does not alter the fact that the law, according to which electric diffusion goes on in both, is the same. Resistance merely affects the magnitude of the proportion of distance, or of time, at which corresponding states of potential are reached in the dielectric of the condenser and in the wire of the cable. In the case of a distance the magnitude of this proportion may be of the order  $10^{-10}$ , in the case of a time it may be of the order  $10^{20}$ .

The whole argument, then, may be summarized in the

\* Math. and Phys. Papers, vol. ii. art. lxxiii.

statement that the motion of the model, and the diffusion of electricity in the dielectric of a condenser, are subject to one and the same mathematical law expressed by equation (1) above.

In conclusion, I would take the liberty of suggesting to the inventors of the model to obtain "hysteresis" diagrams by cyclical loading of the springs. I feel sure that, when published, such diagrams would also prove extremely instructive.

Gordon's College, Aberdeen,  
Sept. 1901.

#### DISCUSSION.

Prof. J. A. FLEMING said he was glad that Dr. Buchanan had drawn attention again to the model because there were points about it which might be further discussed with advantage. After giving a short description of the apparatus, he said that Dr. Buchanan had shown that mathematically the theory of the model was the same as that of electric-current diffusion in a cable, and he suggested that there might be something more than mere mathematical analogy. Prof. Fleming referred to the discussion on the original paper, in which Prof. Ayrton asked in what respect the model served its purpose better than a twisted wire. A twisted wire cannot represent the properties of a dielectric, because if twisted beyond the elastic limits there is a permanent set, and it cannot represent the effect of varying the time of charging a condenser. There is no permanent set in the present model. He should like to know if a dielectric has any real Ohmic conductivity, and suggested that experiments should be made by subjecting a dielectric to constant electric pressure at constant temperature, for years if necessary, and observing whether the curve of current becomes asymptotic to the zero line or to a line parallel to it. The model could be made to represent a conduction as well as a displacement current by so arranging the bottom piston that it could descend but not return. The fact that the movements of the model were similar to the diffusion of current in a cable suggested that the process of conduction in a metal was *similar* to that of displacement in a dielectric.

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VI. *Notes on Gas-Thermometry.*—II. By Dr. P. CHAPPUIS, *Attaché au Bureau International des Poids et Mesures, Sèvres\**.

Messrs. HOLBORN and DAY have published recently in a research on the air-thermometer † the results of a new determination of the expansion of Berlin porcelain between 0° and 1000°.

These experiments are of considerable importance as bearing on the reduction of temperature measurements, in which reservoirs of Berlin porcelain have been employed. I drew attention in a former note ‡ to the fact that part of the divergence found between the results of Messrs. Callendar and Griffiths and of Harker and myself for the boiling-point of sulphur may be attributed to the uncertainty in the values assumed for the expansion of porcelain. I propose now to examine in what way our results would be modified by the introduction of the value for the expansion deduced from the experiments of Messrs. Holborn and Day. I would like at the same time to make clear and correct one or two errors in the note previously mentioned, to which Dr. Chree has been kind enough to draw my attention.

1. Messrs. Holborn and Day have measured the expansion of a rod of unglazed porcelain about 483 mm. in length by the method of the comparator. Their observations are represented in a fairly satisfactory manner by the expression

$$L_t - L_0 = \{2954t + 1.125t^2\}10^{-9}$$

between the limits of temperature +250° and 625°. This function diverges considerably from the observations at 750° and at 875° to again agree better at 1000°. Below 250° it gives values which are too high.

In fact the expansion of Berlin porcelain cannot be represented exactly by a two-term function throughout an interval of temperature exceeding a few hundred degrees.

It follows therefore that an expression for the expansion deduced empirically cannot be applied outside the limits of

\* Read November 22, 1901.

† *Annalen der Phys. und Chem.* 4th series, vol. ii. 1900, p. 505.

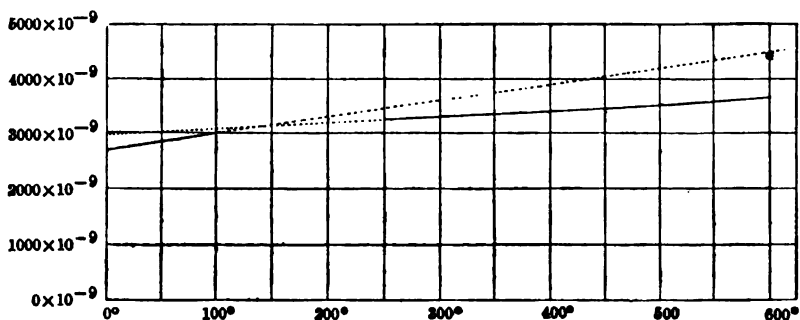
‡ *Phil. Mag.* [5] vol. i. p. 436 (Oct. 1900); *Proc. Phys. Soc.* vol. xvii. p. 358.

the experiments without running the risk of committing serious errors\*.

The following table contains the values of the mean coefficient of expansion between  $0^\circ$  and  $T^\circ$  deduced from our measurements, those of Messrs. Holborn and Wien in 1892 †, and the recent ones of Messrs. Holborn and Day.

T.	Harker & Chappuis, 1898.	Holborn & Wien, 1892.	Holborn & Day, 1900.
$0^\circ$	$2690 \times 10^{-9}$		$2954 \times 10^{-9}$
$100^\circ$	2989		3066
$200^\circ$	(3288)	"	3179
$300^\circ$	(3587)	"	3291
$400^\circ$	(3886)	"	3404
$500^\circ$	(4185)	"	3516
$600^\circ$	(4484)	$4400 \times 10^{-9}$	3629

At the time of our experiments the absence of precise data for the expansion of porcelain compelled us to deduce the values for the higher temperatures by extrapolation of the expression determined between the limits  $0^\circ$  and  $100^\circ$ . The values we thus obtained seemed to be confirmed by Messrs Holborn and Wien, but are not in agreement with the new experiments of Messrs. Holborn and Day.



The above diagram represents the mean coefficients as

\* The case is not the same with platinum, whose expansion measured by Messrs. Holborn and Day by the same method between  $0^\circ$  and  $1000^\circ$  has been found to be  $(8889t + 1.274t^2) 10^{-9}$ . M. Benoit had previously obtained between  $0^\circ$  and  $100^\circ$  in the Fizeau apparatus (*Trav. et Mém. du Bur. Inter.* t. vi. p. 190) the almost identical expression  $(8901t + 1.21t^2) 10^{-9}$ .

Here extrapolation would have led to no serious inaccuracies.

† Holborn & Wien, *Ann. der Phys. und Chem.* Bd. xlvii. p. 121 (1892).

given by our determination and that of Messrs. Holborn and Day.

Since the formula of Messrs. Holborn and Day gives too high values for temperatures below  $250^{\circ}$  the curve should approach ours in this region. It is evident from the diagram that there is therefore no incompatibility between their results and ours, and that they may be considered as approximate values of the same function representing the expansion of Berlin porcelain.

Although there may be doubts as to the identity of the material subjected to experiments in the two cases, and even as to the invariability of the properties of a single specimen, when subjected on several occasions to a lengthy annealing process, it seemed to me interesting to recalculate some of our observations on the boiling-point of sulphur, assuming for the mean coefficient of expansion of the reservoir the value given by the experiments of Messrs. Holborn and Day for the temperature  $445^{\circ}$ . I have kept in this calculation the coefficient obtained by me for nitrogen between  $0^{\circ}$  and  $100^{\circ}$ .

It follows from the introduction of the new values, that the boiling-point of sulphur deduced from our experiments with a porcelain-reservoir thermometer would be lowered  $0^{\circ}5$  C. from  $445^{\circ}2$  to  $444^{\circ}7$ . This number is very close to that obtained by Messrs. Callendar and Griffiths.

It is possible that the measurements in which we employed a reservoir of "verre dur," and which also gave us a value for the boiling-point close to  $445^{\circ}2$ , may be affected by a similar error, but the data at present available for the expansion of this glass at high temperatures do not now permit of the error, if any, being calculated.

I think there would be some interest in redetermining the boiling-point of sulphur, using a bulb of platinum-iridium whose expansion follows a regular and better known law.

2. In the note mentioned above (Proc. Phys. Soc. xvii. p. 356)

I gave the values of the coefficient  $\frac{1}{P_0} \frac{dP}{dt}$  for nitrogen for an initial pressure  $P_0$  of one metre, at different temperatures

comprised between  $0^\circ$  and  $100^\circ$ . Examination of the table of these values shows that the coefficient of nitrogen gradually diminishes and reaches near  $75^\circ$  a limiting value equal to

$$\alpha_{\text{lim}} = 0.003\,673\,80.$$

It may be assumed that starting from this temperature the gas is in the perfect state.

Direct observations of the constants of the nitrogen thermometer having given

$$P_0 = 1.000\,000 \text{ m. and } P_{100} = 1.367\,466 \text{ m.,}$$

we may deduce the initial pressure  $P_0'$ , which should have been observed had the nitrogen retained down to  $0^\circ$  the properties of a perfect gas; that is to say, if the pressure had continued to vary from  $100^\circ$  downwards at the rate of  $0.003\,673\,80$  metre per degree.

We should then have

$$P_0' = P_{100} - 0.003\,673\,80 \times 100 = 1.000\,086 \text{ m.}$$

The thermometer supposed perfect would therefore have at  $0^\circ$  the pressure  $P_0' = 1.000\,086 \text{ m.}$  and at  $100^\circ$   $P_{100} = 1.367\,466 \text{ m.,}$  whence

$$\alpha_1 = \frac{P_{100} - P_0'}{100 P_0'} = 0.003\,673\,48.$$

The values for  $\alpha_1$  and  $P_0'$  here found should be substituted for those given in my previous communication ( $p_0 = 1.000\,063$  and  $\alpha_1 = 0.003\,663\,80$ ).

The divergences between the uncorrected nitrogen scale and the theoretical scale, whose constants have just been calculated and which represents the normal scale of temperatures, are proportional to the temperature measured from  $100^\circ$  and have the following values:—

At	$100^\circ$	.	.	.	.	$0.000$
	$200^\circ$	.	.	.	.	$0.023$
	$300^\circ$	.	.	.	.	$0.047$
	$400^\circ$	.	.	.	.	$0.070$

The difference between these values and those given

previously is too small to be of appreciable practical importance, and our previous conclusions remain unaltered\*.

Sèvres, Jan. 1901.

#### DISCUSSION.

Prof H. L. CALLENDAR said that he was highly gratified to see that the application of the correction for the expansion of the bulb of Dr. Chappuis's gas-thermometer, deduced from Holborn and Day's results, gave a value,  $444^{\circ}\cdot 7$ , for the boiling-point of sulphur in such close agreement with the value  $444^{\circ}\cdot 5$  deduced by Mr. Griffiths and himself in 1890. The agreement was really much closer than appeared at first sight, because the remaining difference of two-tenths of a degree in the results was almost exactly accounted for by the scale difference of the constant-pressure and constant-volume thermometers, according to the theory of Joule and Thomson. It was also interesting to remark that the corrected result found by Dr. Chappuis was in very close agreement with that deduced from their own observations by Messrs. Holborn and Day. Dr. Chappuis had not referred in the present note to the work of Bedford on the expansion of Bayeux porcelain, which he had criticised in a previous paper. A comparison of results would show that Bedford's results agreed very fairly, allowing for the difference of material, with Holborn and Day's from  $200^{\circ}$  to  $600^{\circ}$  C.; and that both differed from those of Dr. Chappuis between  $0^{\circ}$  and  $80^{\circ}$  when extrapolated in a precisely similar manner. It was quite possible, as he (Prof. Callendar) had previously suggested, that the expansion of porcelain between  $0^{\circ}$  and  $100^{\circ}$

\* I take this opportunity of correcting a few mistakes in my previous note (Phil. Mag. *loc. cit.*).

p. 433, line 23.  $\frac{1}{P_0} \frac{dP}{dt}$  instead of  $\frac{1}{P} \frac{dP}{dt}$ .

p. 438, line 7.  $v_t = v_0(1 + (10275t + 3\cdot 24t^2)10^{-9})$ .

p. 438, line 10.  $v_t = v_0(1 + (9715\cdot 6t + 4\cdot 43t^2)10^{-9})$ .

p. 438, line 14.  $v_t = v_0(1 + (9781\cdot 4t + 4\cdot 276t^2)10^{-9})$ .

p. 440, line 23. Read—"the thick part of the tube expands *more* than the thinner part," instead of "*less* than etc."

p. 441, Table, 3rd column, 1st line. Read  $-0\cdot 17$  instead of  $-0\cdot 27$ .

p. 442, Table, 2nd column, 4th line. Read  $+0\cdot 081$  instead of  $+0\cdot 031$

was anomalous. It appeared certain that some anomaly in the expansion at  $800^{\circ}$  was indicated both in the experiments of Bedford and also in those of Holborn and Day. It was also clear that Dr. Chappuis's results for Bayeux porcelain when extrapolated would agree with Bedford's at a temperature a little above  $100^{\circ}$  C., or very nearly at the same point at which his results for Berlin porcelain agreed with those of Holborn and Day.

Dr. R. T. GLAZEBROOK said he had felt for some time that it was of importance that the difference between the results of Callendar and Griffiths and of Chappuis and Harker should be explained, and he was glad that the agreement was now so satisfactory.

Dr. CHREE (communicated subsequent to the meeting).—The "divergence of the nitrogen thermometer from the normal scale" as originally calculated by Dr. Chappuis (Proc. Phys. Soc. vol. xvii. p. 357), amounted practically to  $0^{\circ}\cdot 017$  for each  $100^{\circ}$  interval above  $100^{\circ}$  C.; this number is now replaced at my instance by  $0^{\circ}\cdot 023$ . The "divergence"—or the difference between its old and new values—is small, considering experimental uncertainties. A change, however, from  $\cdot 017$  to  $\cdot 023$ , being an increase of over 30 per cent., is *relatively* somewhat considerable. The change, moreover, represents a fundamental difference in the argument, which ought not to be overlooked, especially in view of the increased accuracy in experiment to which we may reasonably look forward.

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VII. *On Circular Filaments or Circular Magnetic Shells equivalent to Circular Coils, and on the equivalent Radius of a Coil.* By Professor THOMAS R. LYLE\*.

[Plate I.]

1. The magnetic potential of a coil, with current  $C$ , at any point in its axis is given to a high order of approximation by

$$V = 2\pi nC \left( 1 - \frac{x}{\rho} + \frac{\eta^2 x}{24\rho^3} + \frac{\xi^2 - \eta^2}{8\rho^5} a^2 x \right) \quad , \quad \text{I.}$$

if the dimensions of the cross section are small compared with the radius of the coil and the winding is uniform ;

where  $a$  = mean radius,

 $\xi$  = axial breadth, $\eta$  = radial depth,

$x$  = distance of point on the axis from the centre of the coil,

and  $\rho^2 = a^2 + x^2$ .

(See Maxwell, sect. 700.)

Expanding in ascending powers of  $x/a$ ,

$$V = 2\pi nC \left\{ 1 - \frac{x}{a} \left( 1.1 - \frac{3\xi^2 - 2\eta^2}{24a^2} \right) + \frac{x^3}{2a^3} \left[ 1.2 - \frac{3(5\xi^2 - 4\eta^2)}{24a^2} \right] \right.$$
$$\quad - \frac{x^5}{2.4.a^5} \left[ 1.3 - \frac{3.5(7\xi^2 - 6\eta^2)}{24a^2} \right]$$
$$\quad + \frac{x^7}{2.4.6.a^7} \left[ 1.3.5 - \frac{3.5.7(9\xi^2 - 8\eta^2)}{24a^2} \right]$$
$$\quad - \&c. \quad \&c. \Big\}. \dots\dots\dots II.$$

2. The potential  $V'$  of a circular filament concentric and coaxial with the coil of radius  $r$  and with current  $nC$  flowing is given by

$$V' = 2\pi nC \left\{ 1 - \frac{x}{\sqrt{x^2 + r^2}} \right\},$$

\* Read December 13, 1901.

which expanded in ascending powers of  $x/r$  gives

$$V' = 2\pi nC \left\{ 1 - \frac{x}{r} + \frac{x^2}{2r^2} - \frac{1.3.x^3}{2.4.r^3} + \frac{1.3.5.x^4}{2.4.6.r^4} - \&c. \right\}.$$

3. The two potentials  $V$  in (1) and  $V'$  in (2) will be identical provided

$$\begin{aligned} \frac{1}{r} &= \frac{1}{a} \left\{ 1 - \frac{3\xi^2 - 2\eta^2}{24a^2} \right\}, \\ \frac{1}{r^2} &= \frac{1}{a^2} \left\{ 1 - \frac{3(5\xi^2 - 4\eta^2)}{24a^2} \right\}, \\ \frac{1}{r^3} &= \frac{1}{a^3} \left\{ 1 - \frac{5(7\xi^2 - 6\eta^2)}{24a^2} \right\}, \\ &\quad \&c. \qquad \&c. \end{aligned}$$

which equations can all be satisfied to the order of approximation adopted if

$$3\xi^2 - 2\eta^2 = 5\xi^2 - 4\eta^2 = 7\xi^2 - 6\eta^2 = \&c.,$$

that is if  $\xi^2 = \eta^2$

and

$$\frac{1}{r} = \frac{1}{a} \left\{ 1 - \frac{\eta^2}{24a^2} \right\}$$

or

$$r = a \left( 1 + \frac{\eta^2}{24a^2} \right).$$

4. If we expand the potentials in ascending powers of  $a/x$  the same result is arrived at: hence the potentials of a circular coil of square cross section  $(\eta, \eta)$ , mean radius  $a$ , with  $n$  turns and carrying a current  $C$ , and of a circular filament of radius  $a \left( 1 + \frac{\eta^2}{24a^2} \right)$  carrying a current  $nC$ , lying in the median plane of, and coaxial with the coil, are identical at all points on the common axis, and hence by Legendre's theorem identical at all points of space without the coil.

This particular filament, therefore, is equivalent to the coil and can replace it, and the radius of this filament I shall call the *equivalent radius of the coil*, and a coil of square cross section I shall call a *single-shell coil*.

5. In the construction of coils there is no reason why



with ordinary care a very approximately square section could not be attained, and then the above theorem would, as I will explain, simplify the theory of galvanometers and electro-dynamometers, as well as the determination of coil-constants, coefficients of mutual induction, and current-balance constants.

6. A coil of  $n$  turns the axial breadth  $\xi$  of whose section is greater than its radial depth  $\eta$ , of mean radius  $a$  and carrying a current  $C$ , can be replaced by two equal filaments coaxial with the coil, each carrying a current  $\frac{1}{2}nC$ , whose radii are  $a\left(1 + \frac{\eta^2}{24a^2}\right)$ , and which are placed at equal distances  $\beta$  on either side of the median plane of the coil, where

$$\beta^2 = \frac{\xi^2 - \eta^2}{12}.$$

For:

The potential of the two filaments as specified above, at any point on the common axis distant  $x$  from their median plane, is

$$V_2 = 2\pi n C \frac{C}{2} \left\{ 1 - \frac{x - \beta}{\rho_1} + 1 - \frac{x + \beta}{\rho_2} \right\}$$

where

$$\rho_1^2 = r^2 + (x - \beta)^2, \quad \rho_2^2 = r^2 + (x + \beta)^2,$$

$r$  being the radius of either filament. Expanding by Taylor's theorem

$$V_2 = 2\pi n C \left\{ 1 - \frac{x}{\rho} + \frac{\beta^2}{1 \cdot 2} \cdot \frac{3r^2 x}{\rho^5} \right\}$$

(where  $\rho^2 = x^2 + r^2$ )

$$V_2 = 2\pi n C \left\{ 1 - \frac{x}{r} \left[ 1 - \frac{3\beta^2}{2r^2} \right] + \frac{x^3}{2r^3} \left[ 1 - \frac{3 \cdot 5 \cdot \beta^2}{2r^2} \right] - \frac{x^5}{2 \cdot 4 \cdot r^5} \left[ 1 \cdot 3 \cdot - \frac{3 \cdot 5 \cdot 7 \cdot \beta^2}{2r^2} \right] + \&c. \right\}$$

and in order that this may be identical with the axial potential of the coil given in section 1, the following equations have

to be satisfied :—

$$\begin{aligned}\frac{1}{r} \left\{ 1 - \frac{3\beta^2}{2r^2} \right\} &= \frac{1}{a} \left\{ 1 - \frac{3\xi^2 - 2\eta^2}{24a^2} \right\}, \\ \frac{1}{r^3} \left\{ 1 - \frac{3 \cdot 5 \cdot \beta^2}{2r^2} \right\} &= \frac{1}{a^3} \left\{ 1 - \frac{3(5\xi^2 - 4\eta^2)}{24a^2} \right\}, \\ \frac{1}{r^5} \left\{ 1 - \frac{5 \cdot 7 \cdot \beta^2}{2r^2} \right\} &= \frac{1}{a^5} \left\{ 1 - \frac{5(7\xi^2 - 6\eta^2)}{24a^2} \right\}, \\ &\quad \&c. \quad \&c.\end{aligned}$$

It is easily seen that this series of equations will be satisfied to the order of approximation adopted if

$$\frac{1}{r} = \frac{1}{a} \left( 1 - \frac{\eta^2}{24a^2} \right)$$

or

$$r = a \left( 1 + \frac{\eta^2}{24a^2} \right)$$

and

$$\beta^2 = \frac{\xi^2 - \eta^2}{12}.$$

If we expand the potentials in ascending powers of  $a/x$  for the portion of the axis where  $x$  is  $> a$  the same result will be arrived at; hence the potentials of the coil and of the double filament are equal at all points in space external to the coil, and in all calculations (except those bearing on self-induction) the coil can be replaced by this double-shell or filament.

A coil of this type (*i.e.* in which  $\xi > \eta$ ) I shall call a *thick double-shell coil*; the radius of either of the two replacing filaments I shall call the *equivalent radius* of this coil; and the distance  $2\beta$  between the two filaments I shall call the *equivalent breadth* of the coil.

It is obvious now that the coil will be completely specified when its type, its equivalent radius, and its equivalent breadth are given; that all magnetic actions of the coil on systems external to itself will be identical with those of the equivalent filaments; and that all magnetic action on the coil from external systems will be identical with the action of these systems on the filaments, the order of approximation being

up to the fourth power of the dimensions of the section of the coil divided by its radius.

7. A coil of  $n$  turns, the axial breadth  $\xi$  of whose cross section is less than its radial depth  $\eta$ , of mean radius  $a$ , and carrying a current  $C$ , can be replaced by two concentric and coplanar filaments coaxial with and lying in the median plane of the coil, each carrying a current  $\frac{1}{2}nC$ , and whose radii are  $r + \delta$  and  $r - \delta$  respectively, where

$$r = a \left( 1 + \frac{\xi^2}{24a^2} \right),$$

$$\delta^2 = \frac{\eta^2 - \xi^2}{12}.$$

It is unnecessary to give the proof of this, as it follows easily on the same lines as that of the last theorem. A coil of this type might be called a *thin double-shell coil*, while  $r$  as defined above I shall call its *equivalent radius* and  $2\delta$  its *equivalent depth*.

8. In the case of a coil whose cross section is so large that the fourth power of its dimensions divided by its radius cannot be neglected, it is easy to imagine it divided up into portions whose dimensions are small enough for the above theorems to apply, and then to determine the system of filaments that will replace each of these portions. A few extra filaments adds nothing to the difficulty and little to the time required to calculate a coefficient of mutual induction or a current-balance constant, seeing that tables are available by means of which either of these quantities referring to any two coaxial filaments can be quickly determined.

9. The principles embodied in the preceding sections may be established in a totally different way, which is interesting enough to record here.

Its application to a thick double-shell coil ( $\xi > \eta$ ) will be sufficient to explain the method.

If the position of any turn of the coil be defined by  $x$  the distance of its centre from a fixed point on the axis, and  $y$  the radius of the turn, then  $N$  the magnetic flux passing through this turn due to any system whatever of magnets or currents will be a function of  $x$  and  $y$ .

Let us specify a small portion of the coil considered by rectangular coordinates  $p, q$  referred to axes through the centre of the section parallel to the axis of the coil and its radius respectively, then the current round an element  $dp, dq$  of the coil will be  $\frac{nC}{\xi\eta} dp \cdot dq$ .

$\xi$  and  $\eta$  having the same meaning as in previous sections.

The mutual energy of this filament and the external magnetic field will be

$$\frac{nC}{\xi\eta} \left[ N_0 + p \left( \frac{dN}{dx} \right)_0 + q \left( \frac{dN}{dy} \right)_0 + \frac{1}{1 \cdot 2} \left\{ p^2 \frac{d^2 N}{dx^2} + 2pq \frac{d^2 N}{dx dy} + q^2 \frac{d^2 N}{dy^2} \right\} \right] dp \cdot dq,$$

where  $N_0$  is the value of  $N$  at the centre of the section.

Integrating between the limits  $(+\frac{1}{2}\xi, -\frac{1}{2}\xi)$   $(+\frac{1}{2}\eta, -\frac{1}{2}\eta)$  we get the total mutual energy

$$= nC \left\{ N_0 + \frac{1}{24} \left( \xi^2 \frac{d^2 N_0}{dx^2} + \eta^2 \frac{d^2 N_0}{dy^2} \right) + \dots \right\}$$

Again, if we have two equal filaments whose  $p$  and  $q$  coordinates are  $(\alpha, \beta)$ , and  $(-\alpha, \beta)$  respectively, and if a current  $\frac{1}{2}nC$  circulates in each, the mutual energy of the external system and the filaments will be

$$\begin{aligned} & \frac{1}{2}nC \left\{ N_0 + \alpha \frac{dN_0}{dx} + \beta \frac{dN_0}{dy} + \frac{1}{1 \cdot 2} \left[ \alpha^2 \frac{d^2 N_0}{dx^2} + 2\alpha\beta \frac{d^2 N_0}{dx dy} + \beta^2 \frac{d^2 N_0}{dy^2} \right] \right\} \\ & + \frac{1}{2}nC \left\{ N_0 - \alpha \frac{dN_0}{dx} + \beta \frac{dN_0}{dy} + \frac{1}{1 \cdot 2} \left[ \alpha^2 \frac{d^2 N_0}{dx^2} - 2\alpha\beta \frac{d^2 N_0}{dx dy} + \beta^2 \frac{d^2 N_0}{dy^2} \right] \right\} \\ & = nC \left\{ N_0 + \beta \frac{dN_0}{dy} + \frac{1}{2} \left[ \alpha^2 \frac{d^2 N_0}{dx^2} + \beta^2 \frac{d^2 N_0}{dy^2} \right] + \dots \right\}; \end{aligned}$$

but

$$\frac{1}{y} \frac{dN}{dy} = \frac{d^2 N}{dx^2} + \frac{d^2 N}{dy^2}$$

(See Maxwell, section 703);

then the energy of the two filaments reduces to

$$nC \left\{ N_0 + (\beta y_0 + \frac{1}{2}\alpha^2) \frac{d^2 N_0}{dx^2} + (\beta y_0 + \frac{1}{2}\beta^2) \frac{d^2 N_0}{dy^2} + \&c. \right\};$$

and in order that this may be identical with the expression for the energy of the coil

$$\beta y_0 + \frac{1}{2} \alpha^2 = \frac{\xi^2}{24} \quad \text{and} \quad \beta y_0 + \frac{1}{2} \beta^2 = \frac{\eta^2}{24}.$$

Solving the second equation we have to the order of approximation adopted

$$\beta = \frac{\eta^2}{24 y_0},$$

and then from the first

$$\alpha^2 = \frac{\xi^2 - \eta^2}{12};$$

but the radius of the replacing filaments being  $y_0 + \beta$  is

$$= y_0 \left( 1 + \frac{\eta^2}{24 y_0^2} \right),$$

and their distance apart is  $2\alpha$  where  $\alpha^2 = \frac{\xi^2 - \eta^2}{12}$  as before.

As an illustration of this method of treating the problem, the following case may be considered:—

Let the external field be uniform and the axis of the coil parallel to the lines of force of the field.

The mutual energy is  $C \Sigma N$ , where  $N$  is the magnetic flux through any one turn.

But  $C \Sigma N = (n \cdot C \cdot H) \times \text{mean area of the coil}$

$$= nCH \times \pi \left( a^2 + \frac{\eta^2}{12} \right)$$

as is easily shown by integration:  $a$  being the mean radius as before.

In this case the equivalence of the filaments replacing a thick double shell or a single shell to their corresponding coils is obvious.

For a thin double shell the mean area of the two filaments is

$$\begin{aligned} & \pi(r^2 + \delta^2) \\ &= \pi \left\{ a^2 + \frac{\xi^2}{12} + \frac{\eta^2 - \xi^2}{12} \right\} \\ &= \pi \left\{ a^2 + \frac{\eta^2}{12} \right\}, \end{aligned}$$

and this is again equal to the mean area of the corresponding coil.

*Applications of the foregoing Principles.*

10. The constant of a single-shell galvanometer-coil corrected for cross section is  $2n\pi/r$  where  $r$  is its equivalent radius ; while that of a thick double-shell coil is

$$\frac{2n\pi}{r} \left( 1 - \frac{3}{2} \frac{\beta^2}{r^2} \right),$$

where  $r$  is its equivalent radius and  $2\beta$  its equivalent breadth, and that of a thin double-shell coil is

$$\frac{2n\pi r}{r^2 - \delta^2} \text{ or } \frac{2n\pi}{r} \left( 1 + \frac{\delta^2}{r^2} \right),$$

where  $r$  is its equivalent radius and  $2\delta$  its equivalent depth.

11. The magnetic force  $H$  at any point on the axis of the three types of coils distant  $x$  from their centres is given by

$$H = 2\pi n C \frac{r^2}{\rho^3} \quad \text{for a single shell,}$$

$$H = 2\pi n C \frac{r^2}{\rho^3} \left\{ 1 + \frac{3}{2} \cdot \frac{4x^2 - r^2}{\rho^2} \beta^2 \right\} \quad \text{for a thick double shell,}$$

and

$$H = 2\pi n C \left\{ \frac{r^2}{\rho^3} + \frac{1}{2} \cdot \frac{2x^4 - 11x^2r^2 + 2r^4}{\rho^7} \delta^2 \right\} \quad \text{for a thin double shell,}$$

where  $\rho^2 = r^2 + x^2$ .

It will be noticed that in the expression for the axial  $H$  of a thick double-shell coil the second term, depending on the equivalent breadth, will disappear when  $x = r/2$ : hence a Helmholtz galvanometer made of equal coils of either the first or second type which are placed at *half their equivalent radii* apart is an ideal instrument of its kind, as the corrections both for the cross sections of its coils and for the length of its needle disappear from its constant.

12. In practice the equivalent radius of a coil may be determined in one or other of three ways.

a. By measurement of the mean radius and cross section and substituting the values so obtained in the expressions given for the equivalent radii of the three types of coils in §§ 4, 6, and 7.

b. By comparison by Bosscha's method with a standard coil, preferably a single-shell one, whose equivalent radius has been carefully determined by method a.

c. By a second electrical method which I will presently describe.

13. It is important to note that the comparison of two single-shell coils by Bosscha's method gives directly the ratio of their equivalent radii, no corrections having to be added if the length of the small needle at the common centre of the two coils be neglected. (This latter correction is, however, larger than, I think, many people imagine and should be applied in most cases, taking five-sixths of the actual length of the small magnet for the distance between its poles\*.)

Thus if  $R_1$  and  $R_2$  be the resistances of the parallel branches in which the two coils  $r_1, n_1$  and  $r_2, n_2$  are included when the needle at their common centre is unaffected, then

$$\frac{r_1}{r_2} = \frac{n_1 R_2}{n_2 R_1};$$

and if the distance  $2\lambda$  between the poles of the small magnet be taken into account (see Maxwell, § 711),

$$\frac{r_1}{r_2} = \frac{n_1 R_2}{n_2 R_1} \left\{ 1 + \frac{3}{4} \lambda^2 \left( \frac{1}{r_1^3} - \frac{1}{r_2^3} \right) \right\},$$

where for  $r_1$  and  $r_2$  on the right side the mean radii  $a_1$  and  $a_2$  got by approximate measurement may be substituted.

In general we have

$$\frac{R_1}{R_2} = \frac{G_1}{G_2} \left\{ 1 + \frac{3}{4} \lambda^2 \left( \frac{1}{a_1^3} - \frac{1}{a_2^3} \right) \right\},$$

where  $R_1, R_2$  are the resistances of the two parallel branches in which the coils lie, and  $G_1, G_2$  their galvanometer constants given in terms of equivalent radius, breadth or depth in § 10.

14. The proposed electrical method of measuring the equivalent radius of a coil will be easily understood from the following. If, with the apparatus used in Bosscha's method

\* See W. Hallock and F. Kohlrausch, *Wied. Ann.* xxii. p. 411, or abstract in *Phil. Mag.* [5] vol. xviii. p. 390, "On the Distance apart of the Poles of a Magnet."

for determining the ratio of the equivalent radii of two coils, some arrangement be made by means of which the smaller coil can slide to either side of the larger one, still remaining coaxial with and parallel to it, then if the former be moved a distance  $x$  to either side, and if the resistances be readjusted so that the magnet at the centre of the large coil is not affected, we have

$$\frac{n_1}{r_1 R_1'} = \frac{n_2 r_2^2}{R_2' (r_2^2 + x^2)^{\frac{3}{2}}}, \quad \dots \quad (\text{I.})$$

if the coils be single-shell ones, where  $R_1'$  and  $R_2'$  are the new resistances in the parallel branches. If with the same resistances  $R_1'$  and  $R_2'$  in the branches, balance is obtained with the small coil first at one side and then at the other, the distance between the two positions of the small coil will be  $2x$ ; and as the ratio of  $r_1$  to  $r_2$  determined by the method in the last section is known and given by

$$\frac{r_1}{r_2} = \frac{n_1 R_2}{n_2 R_1}, \quad \dots \quad (\text{II.})$$

we can from equations I. and II. determine both  $r_1$  and  $r_2$  in terms of  $2x$  and the two ratios of resistances.

The most sensitive position in which to place the small coil is that at which  $dH/dx$  is a maximum, that is when the small coil is at a distance from the needle (and the plane of the large coil) equal to one half of its equivalent radius.

For this position, equation I. becomes

$$\frac{n_1}{r_1 R_1'} = \frac{n_2}{r_2 R_2'} \frac{8}{5\sqrt{5}};$$

so that

$$\frac{R_1'}{R_2'} = \frac{5\sqrt{5}}{8} \frac{R_1}{R_2},$$

$R_1$  and  $R_2$  being the resistances in Bosscha's comparison method.

Hence we arrange the resistances  $R_1'$  and  $R_2'$  so that their ratio is  $5\sqrt{5}/8$  times the resistance ratio in Bosscha's method, adjust the small coil accurately first on the east and then on the west of the large coil so that the magnet is unaffected; the distance between these two positions is the equivalent radius of the small coil. Four determinations of  $r_2$  can be made by varying the relative aspects of the faces of



the two coils, and increased sensitiveness can, if desired, be obtained by using a compensating magnetic system to partly neutralize the earth's field. This is, however, rarely necessary as the method is exceedingly sensitive. It would be an advantage, however, when extreme accuracy is required, as one could then work with smaller currents, and so minimize the variation of the resistances due to heating.

15. Similar treatment can obviously be applied to the large coil. Thus when the coplanar resistance ratio is now changed to  $R_1''/R_2''$  so that  $\frac{R_1''}{R_2''} = \frac{8}{5\sqrt{5}} \frac{R_1}{R_2}$ , and the large coil moved to equilibrium positions east and west of the small coil and the needle, the distance between these two positions of the large coil will be equal to its equivalent radius. This determination can then be used to check the one made by moving the small coil.

16. Plate I. shows a diagrammatic section of the apparatus I have used for the above purpose.

A is a strong wooden base on levelling-screws. B is a strong flat bar which can slide parallel to the length of the base, and can be clamped in any position to a slow-motion screw *a* of small pitch and having a small range. To B is attached an upright piece C, one of whose faces is very carefully planed and set perpendicular to the upper surface of B and to the line of motion of B. To C the larger coil is to be attached by means of a clamp as in the diagram. A pair of uprights F and another pair F' rise from the base, each pair being joined near the top by a cross-piece. In the upper sides of these cross-pieces rectangular slots are cut in which a strong bar D can slide parallel to the other slide B. D can be clamped in any position to the slow-motion screw *b* which is of fine pitch and has a short range. To the lower side of D is fixed a piece E, one of whose faces is carefully planed and set perpendicular to D. To this piece the smaller coil is to be attached. Resting on the upper ends of the four pillars F and F' is a brass table fitted with short levelling-screws for carrying the magnetometer. The telescope and scale are set up on the left side, and to the opposite ends of the beams B and D are attached (as in the diagram) carefully ruled glass millimetre-scales S and S' by means of which, with the

assistance of two micrometer-microscopes, the motion of B and of D and so of either coil in the axial direction can be accurately measured.

There is little difficulty in setting up and centering the coils, but I have found the following method convenient :—The magnetometer being replaceable in a given position, the axial line through the centre of the magnet is determined by directing a horizontal telescope whose line of sight is parallel to D to the centre of the magnet. A small scriber which takes the place of the magnetometer is now adjusted so that the image of its point coincides with the cross wires of the telescope. Across one face of each coil a fine wire is stretched along a diameter by means of a centre square and the middle points of the diameters marked. The coils are now clamped in position so that the middle points of these diametral wires coincide with the point of the scriber.

17. In measuring the equivalent radii of the coils we must first determine the ratio of the resistances that are included in the parallel arms containing the coils when their actions on the needle balance each other, the needle being at the common centre of the coils. The adjustment of the coils so that the needle is at their common electrical centre is of importance, and is managed as follows. First adjust by eye, then arrange the resistances so that with currents flowing the needle is not affected; now, by means of the slow-motion screws attached to each slide, the coils can in turn be moved axially until they both have maximum magnetic effect on the needle. When this has been effected in the usual way for adjusting for a maximum or minimum, we know that the centre of the needle lies at the common electrical centre of the two coils.

The resistance ratio of the branches will now require slight readjustment, and then its value  $R_1/R_2$  is determined as Lord Rayleigh\* and Mrs. Sidgwick have done, by means of a specially arranged Wheatstone's bridge. The resistances in the branches are then changed to  $R_1'$  and  $R_2'$ ,

$$\text{where} \quad \frac{R_1'}{R_2'} = \frac{5\sqrt{5}}{8} \frac{R_1}{R_2},$$

\* Phil. Trans. 1884.

if both the coils are single-shell ones, and the small coil moved first to one side then to the other to positions in which with currents flowing the needle is not affected. The distance between these two positions is the equivalent radius of the small coil.

The small coil having been replaced at the centre, the resistances in the branches are again changed to  $R_1''$  and  $R_2''$ , where

$$\frac{R_1''}{R_2''} = \frac{8}{5\sqrt{5}} \frac{R_1}{R_2};$$

and the large coil is now moved, first to one side and then to the other, to positions of equilibrium. The distance between these two positions will be the equivalent radius of the large coil.

As the ratio  $R_1/R_2$  determined in the first part of this process gives us (see § 13) the ratio of the equivalent radii of the two coils,

$$\frac{r_1}{r_2} = \frac{n_1 R_2}{n_2 R_1},$$

this value of the ratio  $r_1/r_2$  can be used as a check on the ratio of the values of  $r_1$  and  $r_2$  determined separately.

18. If both coils be thick double-shell ones the second resistance-ratio, that is the one ( $R_1'/R_2'$ ) used in measuring  $r_2$ , must be adjusted so that

$$\frac{R_1'}{R_2'} = \frac{5\sqrt{5}}{8} \left(1 - \frac{3}{2} \frac{\beta_2^2}{a_2^2}\right) \frac{R_1}{R_2};$$

and the third resistance-ratio  $R_1''/R_2''$ , i. e. the one used in measuring  $r_1$ , must be adjusted so that

$$\frac{R_1''}{R_2''} = \frac{8}{5\sqrt{5}} \left(1 - \frac{3}{2} \frac{\beta_1^2}{a_1^2}\right) \frac{R_1}{R_2},$$

where  $2\beta_1$  and  $2\beta_2$  are the *equivalent* breadths of the two coils and  $a_1$  and  $a_2$  their approximate mean radii.

For any combination of two coils of different types, the factors that have to be applied to the coplanar resistance-ratio to get the second and third ratios can easily be deduced from the expressions given in §§ 10, 11.

18a. The length of the small needle in the magnetometer should be known, and the factors for getting the second and

third resistance-ratios from  $R_1/R_2$  should be corrected for it. The correction to be applied to each factor will be the same for all kinds of coils.

When the coils and needle are coplanar there is equilibrium, provided

$$\frac{2\pi n_1}{R_1 r_1} \left(1 + \frac{3}{4} \frac{\lambda^2}{r_1^2}\right) = \frac{2\pi n_2}{R_2 r_2} \left(1 + \frac{3}{4} \frac{\lambda^2}{r_2^2}\right),$$

where  $2\lambda$  is the distance between the poles of the needle. (See Maxwell, section 711.)

When the small coil is displaced along the axis a distance = half its radius, there will be equilibrium provided the resistances are changed to  $R_1'$  and  $R_2'$  so that

$$\frac{2\pi n_1}{R_1' r_1} \left(1 + \frac{3}{4} \frac{\lambda^2}{r_1^2}\right) = \frac{2\pi n_2}{R_2' r_2} \frac{8}{5 \sqrt{5}};$$

for as the needle is now in the Gaugain position with respect to the small coil, its length disappears from the expression for the torque exerted by the small coil on the needle.

Hence from the two equations above we get

$$\frac{R_1'}{R_2'} = \frac{R_1}{R_2} \left(1 + \frac{3}{4} \frac{\lambda^2}{r_2^2}\right) \frac{5 \sqrt{5}}{8}.$$

Similarly it may be shown for the other factor that

$$\frac{R_1''}{R_2''} = \frac{R_1}{R_2} \left(1 + \frac{3}{4} \frac{\lambda^2}{r_1^2}\right) \frac{8}{5 \sqrt{5}};$$

so that the factors in § 18 would become

$$\frac{5 \sqrt{5}}{8} \left(1 - \frac{3}{2} \frac{\beta_2^2}{a_2^2}\right) \left(1 + \frac{3}{4} \frac{\lambda^2}{a_2^2}\right),$$

and

$$\frac{8}{5 \sqrt{5}} \left(1 - \frac{3}{2} \frac{\beta_1^2}{a_1^2}\right) \left(1 + \frac{3}{4} \frac{\lambda^2}{a_1^2}\right);$$

and similarly in other cases.

19. The practical application of the above plan of measuring the equivalent radii of coils offers no difficulty to a careful experimenter. The method is accurate and sensitive, its accuracy depending (1) on the accuracy of the comparison and adjustment of resistances; (2) on the slide-apparatus being well enough made to give very nearly true axial

motion to the coils with a minimum of friction; (3) on the delicacy of motion given by the slow-motion screws to the sliding-bars.

The accurate measurement of the displacement of a coil offers no difficulty.

In regard to (1), the arrangement used by Lord Rayleigh and Mrs. Sidgwick to compare the mean radii of the coils of their current-balance leaves nothing to be desired. The apparatus I have described is the one I have used, and is not necessarily of the most suitable design. The slow-motion attachments to the sliding-bars are not altogether a success, and will have to be modified. The motion realized was not delicate enough and was rather jerky, so that I could rarely adjust the displaced coil in an exact equilibrium position. The necessity for a sensitive slow motion will appear from the following.

Two ordinary galvanometer-coils were being measured, one, the larger, of 36 turns and resistance nearly 1 ohm, the other of 30 turns and resistance a little over half an ohm. The battery-power used was three secondary cells with a resistance of 20 ohms included in the circuit. When the small coil was very near the equilibrium position ( $\frac{1}{2}$  from the large coil), a motion of .016 cm. of the small coil caused a motion of the needle represented by 14 millimetres on a scale 40 cm. from the mirror. The little magnet was swinging in the earth's field slightly neutralized so that it made one swing in 2 seconds. Thus 1 mm. motion of the scale in the telescope corresponded very nearly to a motion of one-hundredth of a millimetre of the coil, and at a distance of 40 cm. from the mirror a half-millimetre scale could be used with comfort, and each half millimetre divided into tenths.

In order to indicate the degree of accuracy obtainable, as well as the necessity of having the motion of the slide-bars as frictionless as possible, I will quote the following results for the equivalent radius of a small galvanometer-coil obtained with a rough preliminary apparatus.

In this apparatus the slow-motion screw could only apply a thrust to the slide-bar at the end near the observer, the bar being drawn back by hand, when it was necessary to do so.

The two equilibrium positions of the small coil are indicated by A and B, A being on the side of the magnetometer furthest from the observer.

1. Coil adjusted at A so as to give a balance, then drawn to other side of magnetometer and adjusted similarly at B. Distance A to B = 8.7280 cm.
2. Similarly, but pushing the coil from B to A position. Distance B to A = 8.7258 cm.
3. Same as 1. „ A to B = 8.7278 cm.
4. Same as 2. „ B to A = 8.7255 cm.

It will be seen that there is a nearly constant difference between the results obtained when the slide-bar is drawn towards the observer from the A to the B position, and when it is thrust from the observer from the B to the A position. There was, I found, considerable friction between the slide-bar and the far upright which fully accounted for this discrepancy, as the force of a few pounds was sufficient to compress that part of the bar (it was not a very thick one) between the coil and the far upright, in which it slid, by an amount equal to the discrepancy.

20. From the theory established in the early sections of this paper, it is obvious that the determination of the mutual inductance of any two coaxial circular coils is reduced to that of coaxial circular filaments; and in this method no terms are neglected of order lower in small quantities than the fourth power of the ratio of the cross section to the radius.

Hence by using Maxwell's tables (see Maxwell, Chap. xiv.

Appendix) for  $\log \frac{M}{4\pi \sqrt{r_1 r_2}}$  as a function of  $\gamma$ , where

$$\sin^2 \gamma = \frac{4r_1 r_2}{(r_1 + r_2)^2 + x^2},$$

$r_1$  and  $r_2$  being the radii of the filaments, and  $x$  the distance between their planes, we can quickly and accurately determine the mutual induction of two coils.

21. For single-shell coils of equivalent radii  $r_1$  and  $r_2$  and distance  $x$  apart the process is very expeditious, for  $M$ , determined as in § 20, has only to be multiplied by  $n_1 n_2$  to get the mutual inductance of the coils.

22. To determine the mutual inductance of two double-shell coaxial coils, we replace the coils by their equivalent filaments, determine the  $M$ 's as in § 20 for the four pairs got by combining a filament of one coil with a filament of the other, and multiply the mean of these by  $n_1 n_2$ .

For, the mutual inductance of two coils being their mutual energy when unit current is circulating in each, and as unit current in a double-shell coil is replaced by a current of  $\frac{1}{2}n$  in each of its equivalent filaments, then, if  $\widehat{ab}$  be Maxwell's  $M$  for two coaxial filaments  $a$  and  $b$ , and if  $a a'$  be the pair equivalent to one coil and  $b b'$  be the pair equivalent to the other, the mutual energy of currents of  $\frac{1}{2}n$  circulating in  $a$  and  $a'$  with respect to currents  $\frac{1}{2}n'$  circulating in  $b$  and  $b'$  will be

$$\frac{1}{2}nn'\{\widehat{ab} + \widehat{a'b} + \widehat{ab'} + \widehat{a'b'}\}$$

$= nn' \times \text{mean of the four } M\text{'s.}$

Thus four determinations of an  $M$  are required in the case of double-shell coils, but this does not involve four times the labour of a single determination if the four calculations are worked concurrently, as corresponding numbers in the four will be found on the same or consecutive pages of a logarithm book.

23. As an example I will give the leading figures in the calculation of the mutual inductance of Rowland's coils A and B used in his determination of the ohm.

Coil A.....  $a_1 = 13.710$ ,  $\xi_1 = .84$ ,  $\eta_1 = .90$ ,  $n_1 = 154$ .

Coil B.....  $a_2 = 13.690$ ,  $\xi_2 = .84$ ,  $\eta_2 = .90$ ,  $n_2 = 154$ .

Distance apart = 6.534.

So both coils are thin double-shell ones and are specified in the notation used by

$$A \left\{ \begin{aligned} r_1 &= a_1 \left( 1 + \frac{\xi_1^2}{24a_1^2} \right) = 13.7121, \\ \delta_1^2 &= \frac{\eta_1^2 - \xi_1^2}{12} = .0087, \quad \delta_1 = .0933. \end{aligned} \right.$$

$$B \left\{ \begin{aligned} r_2 &= a_2 \left( 1 + \frac{\xi_2^2}{24a_2^2} \right) = 13.6921, \\ \delta_2 &= \delta_1 = .0933. \end{aligned} \right.$$

Hence the radii of the filaments equivalent to A being

$$r_1 + \delta_1 \text{ and } r_1 - \delta_1 \text{ are}$$

$$13.8054 \text{ and } 13.6188$$

and to B are

$$13.7854 \text{ and } 13.5988,$$

so we have to determine the four M's where

	Radii.	Distance.
1...	13.8054 and 13.7854	6.534
2...	13.8054 „ 13.5988	6.534
3...	13.6188 „ 13.7854	6.534
4...	13.6188 „ 13.5988	6.534

From which we get (see Maxwell, chap. xiv.)

$$\gamma_1 = 76^\circ 40' \frac{182}{300}, \quad \gamma_2 = 76^\circ 34' \frac{288}{302}, \quad \gamma_3 = 76^\circ 35' \frac{29}{302}, \quad \gamma_4 = 76^\circ 30' \frac{12}{303}$$

$$M_1 = 161.2805$$

$$M_2 = 159.1388$$

$$M_3 = 159.1642$$

$$M_4 = 157.1594$$

$$\text{Mean } M = 159.1857.$$

$$\text{Mutual Inductance} = n_1 n_2 M$$

$$= 3775250.$$

Rowland's value for the same pair of coils was

$$3775500.$$

24. In determining the constant of a current-balance of the type used by Lord Rayleigh and Mrs. Sidgwick in their determination of the electrochemical equivalent of silver, and of which the coils should preferably be single-shell ones, we should first determine the equivalent radii of the two large coils and of the suspended coil by the method I have explained above, which involves in the first instance determining the ratios of these equivalent radii.

It is possible also to realize an accuracy, if due care be taken, that is comparable with what can be obtained in measuring a straight line by the well-known methods.

We can now imagine the coils replaced by their equivalent filaments and calculate for each pair of attracting or repelling



filaments the value of the parameter  $\gamma$  where

$$\sin^2 \gamma = \frac{4r_1 r_2}{(r_1 + r_2)^2 + x^2} \quad \text{as before.}$$

From Lord Rayleigh's Table \* we get the value of

$$\log \left( \frac{\sqrt{r_1 r_2} dM}{x dx} \right)$$

corresponding to each value of  $\gamma$  and thence  $\frac{dM}{dx}$  for the pair of filaments considered. The total force between the four mutually attracting or repelling pairs of filaments is  $= \frac{1}{2} n_1 n_2 C^2 \times$  sum of the four values of  $\frac{dM}{dx}$ .

25. As an example I give the leading figures in the calculation of the constant of the current-balance used by Lord Rayleigh and Mrs. Sidgwick.

Particulars of the large coils :—

$$a_1 = a_1' = 24.81016$$

$$\xi_1 = 1.5, \quad \eta_1 = 1.29.$$

$$\text{Number of turns on each} = n_1 = 225.$$

It is a thick double-shell coil and its equivalent radius  $r_1$

$$\text{being} = a_1 \left( 1 + \frac{\eta_1^2}{24a_1^2} \right),$$

$$\text{is} = 24.81295.$$

Its equivalent breadth  $2\beta$  is given by

$$\beta_1^2 = \frac{\xi_1^2 - \eta_1^2}{12},$$

hence

$$\beta_1^2 = .0490 \quad \text{and} \quad \beta_1 = .221.$$

The distance between the median planes of the two large coils was 25 cms.

Particulars of the suspended coil :—

$$a_2 \text{ approximately} = 10.25,$$

$$\xi_2 = 1.3843, \quad \eta_2 = .9690,$$

$$\text{Number of turns } (n_2) = 242.$$

\* Phil. Trans. 1884.

It is also a thick double-shell coil whose equivalent radius ( $r_2$ ) will be determined by Bosscha's method and whose equivalent breadth  $2\beta_2$  is given by

$$\beta_2^2 = \frac{\xi_2^2 - \eta_2^2}{12},$$

hence

$$\beta_2 = .0814 \text{ and } \beta_2 = .285.$$

It was found that when balance was obtained in Bosscha's comparison method with resistances  $R_1$  and  $R_2$  in the parallel arms containing either of the large coils and the small coil respectively, that the mean value of

$$\frac{R_3}{R_1} \text{ was } = 2.60070.$$

Hence (see §§ 10 and 13) as the ratio of the equivalent radii

$$= \frac{r_1}{r_2} = \frac{n_1 R_2}{n_2 R_1} \left\{ 1 - \frac{3}{2} \left( \frac{\beta_1^2}{a_1^2} - \frac{\beta_2^2}{a_2^2} \right) \right\}$$

we get

$$\frac{r_1}{r_2} = \frac{225}{242} \times 2.60070 \times 1.001044,$$

or

$$r_2 = \frac{24.81295}{2.42053} = 10.25104.$$

The force between the suspended and one of the fixed coils is now equal to the sum of the four forces between two coaxial circular filaments of radii 24.81295 and 10.25104 [each small filament carrying current  $= \frac{1}{2}n_2 C$  and each large filament carrying current  $\frac{1}{2}n_1 C$ ] at the four different distances

$$x + \beta_1 + \beta_2, \quad x - \beta_1 - \beta_2,$$

$$x + \beta_1 - \beta_2, \quad x - \beta_1 + \beta_2,$$

that is 13.006, 11.994, 12.436, 12.564.

The parameter  $\gamma$  for each of these pairs will be

$$58^\circ 31'.74, \quad 59^\circ 23'.88, \quad 59^\circ 1'.29, \quad 58^\circ 54'.69,$$

which give respectively for  $\frac{dM}{dx}$  the values

$$1.032198, \quad 1.055872, \quad 1.046662, \quad \text{and} \quad 1.043648,$$

whose mean value is

$$1.044595.$$

Lord Rayleigh's value for the same was

$$1.044627.$$

26. If, in the above calculation, I made allowance for the length of the small magnet used in comparing the equivalent radii of the coils, there would be a very appreciable difference in the result even if the needle were very short. I do not know the length of the needle actually used by Lord Rayleigh\*, but if it was half a centimetre long or 4 mm. between its poles  $M$  would be

$$1.045154 \text{ instead of}$$

$$1.044595,$$

that is the correction would be 54 in 100,000. For other lengths the correction can be got as it varies as the square of the distance between the poles of the needle. Thus, if the pole distance were only 1 mm., the correction would be more than 3 parts in 100,000, and if it were 3 mm. (a fairly short needle) the correction would be 3 parts in 10,000, which would affect the measurement of current to the extent of  $1\frac{1}{2}$  parts in 10,000.

27. In the case of a standard of mutual inductance of which the coils are very approximately single-shell ones whose equivalent radii have been accurately determined by the electrical method, it might be worth while taking account of the effect of change of temperature on the value of  $M$ .

If the distance-piece between the two coils be of the same material as that on which the coils are wound, and whose coefficient of linear expansion  $\alpha$  is nearly equal to that of the copper wire in the coils, then at once

$$M_t = M_0(1 + \alpha t),$$

seeing that  $M$  is a homogeneous function of  $r_1$ ,  $r_2$ , and  $x$  of one dimension.

\* In the discussion on the paper, when read before the Physical Society, Lord Rayleigh pointed out that the length of the needle was one-tenth of an inch, and the error due to the neglect of the length was less than one part in ten thousand.

For a current-balance in which the two large coils are wound on the same frame, and the suspended coil wound on a ring of the same material whose coefficient of expansion is nearly equal to that of copper, the temperature-coefficient of its constant vanishes seeing that  $\frac{dM}{dx}$  is a homogeneous function of  $r_1 r_2$ , and  $x$  of no dimensions.

#### DISCUSSION.

The Secretary read a letter from Lord RAYLEIGH, in which he stated that the length of the magnet used in obtaining the constant of the current balance used in the determination of the electro-chemical equivalent of silver was one-tenth of an inch, and the error due to neglecting this was less than one part in ten thousand.

Mr. W. WATSON expressed his interest in the method because it reduced the ordinary arithmetical calculations, and drew attention to some advantages of the practical applications.

Prof. S. P. THOMPSON said that it was a useful step to reduce the action of a rectangular coil to that of two filaments. In the case of a tangent galvanometer with one coil, if the channel is cut to take nine turns axially and eleven radially, then the equivalent radius is equal to the mean radius.

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VIII. *Multiple Transmission Fixed-Arm Spectroscopes.* By  
W. CASSIE, M.A., *Professor of Physics in the Royal  
Holloway College* \*.

VARIOUS forms of spectroscope have been devised to diminish the number of prisms required for great dispersion by using each prism more than once. Contrivances for reflecting the beam of light back through a prism or train of prisms a second time by means of a mirror or a reflecting prism have been used by many observers. An instrument has been devised by Prof. Wadsworth in which the beam is sent six times through one prism by the use of seven mirrors.

The spectroscopes described in the present paper secure many transmissions of the beam through one or two prisms by the use of a principle which will be best explained by describing the instruments themselves.

I.

The first form of instrument I have to describe, which is in some respects the most satisfactory of the first three, is made with two half-prisms each silvered on one side. Figs. 1 and 2 (p. 118) show the essentials of the instrument, fig. 1 in plan and fig. 2 in elevation.

A is the collimator, B the telescope.  $abc$  and  $def$  are two equal half-prisms silvered on the faces  $ac$  and  $df$  and placed with their faces vertical. The beam of light, after emerging from the collimator A, passes under the prism  $abc$  and strikes the prism  $def$  near the lower edge of the face  $de$ . This prism is so placed that the beam entering at  $de$  is reflected almost normally at the silvered face  $df$ , and comes out again at the face  $de$ . Now this beam is not horizontal in direction, but is slightly inclined upwards. The consequence is that the beam returning after emergence from  $de$  can be caused to strike the prism  $abc$  on the lower part of the face  $ab$ . This prism also is placed so that the beam is reflected almost normally at the silvered face  $ac$ , and after emerging from  $ab$  again strikes  $de$  at a place higher than at first; and so travels backwards and forwards between the two prisms,

\* Read November 22, 1901.

gradually climbing upwards until at last the beam from  $a b$  passes over the top of the prism  $d e f$  and enters the telescope B. Each reflexion through a half-prism is equivalent to transmission with minimum deviation through a prism whose refracting

Fig. 1.

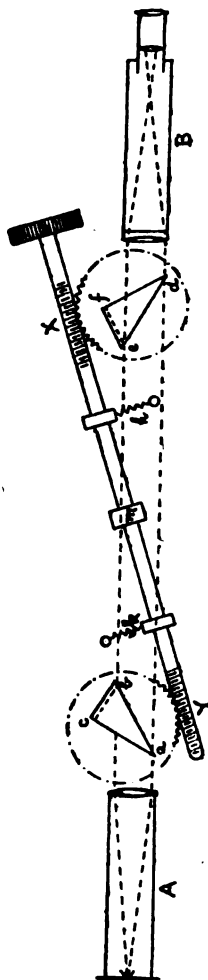
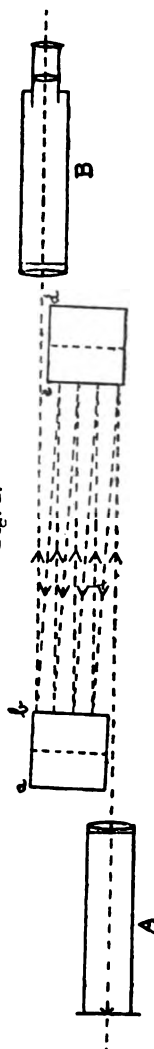


Fig. 2.

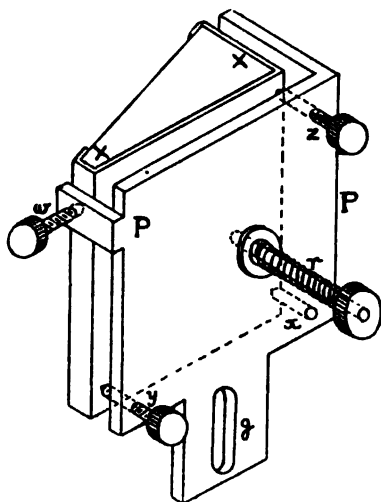


angle is twice that of the half-prism. So that this arrangement is equivalent to a train of as many prisms as there are

reflexions of the beam. The loss of light can be reduced to a minimum by choosing the angles of the prisms so that the light is incident at the angle of polarization.

The adjustment for light of different refrangibilities is secured by turning the prisms in opposite directions so that they are always inclined to the beam of light at equal angles. This is done by supporting the prisms on disks with cogged edges, represented by the circles surrounding them in fig. 1, and having a rod  $XY$  with tangent-screws pressed against these disks by springs  $h, k$ . The rod  $XY$  can be turned about the point  $m$  so as to remove the tangent-screws from the disks for a quick motion of the prisms. The prisms are attached to the disks by mountings which admit of their accurate adjustment. When the instrument has been adjusted for light of one refrangibility, it is adjusted for all refrangibilities; and the whole spectrum can be made to cross the field of view by turning the head of the tangent-screws.

Fig. 3.



The mounting of a prism is shown in fig. 3. The prism is fixed in a brass cell  $X$  which is attached by springs and screws to the upright plate  $P$ . From the back of the prism-cell a rod  $r$  passes freely through a hole in the plate  $P$ , and is sur-

rounded by a spiral spring which presses the cell against the fixed point  $x$  (which enters a slight depression in the back of the cell) and the points of the screws  $y$  and  $z$ . The cell is pressed against the point of the screw  $w$  by a spring on the opposite side. The plate  $P$  is supported with freedom for adjustment by a bolt and nut passing through the slot  $g$ .

The breadth of the beam which can be used is limited horizontally only by the breadth of the face of the prism; but vertically the beam must be narrow if a number of reflexions are required. Thus the resolving power of the instrument depending, as it does, on the horizontal breadth of the beam, is not affected by this restriction. The resolving power is that of a train of as many complete prisms as there are reflexions in the half-prisms.

The beam does not traverse the prisms exactly in a principal plane. But the smallness of this obliquity and the narrowness of the beam in a vertical direction make any such effect of small consequence. Moreover, the obliquity can be indefinitely diminished by increasing the distance between the prisms.

## II.

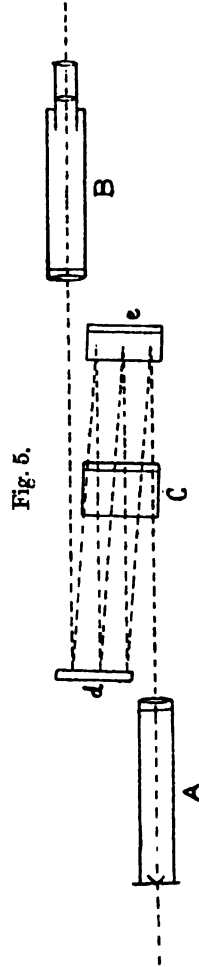
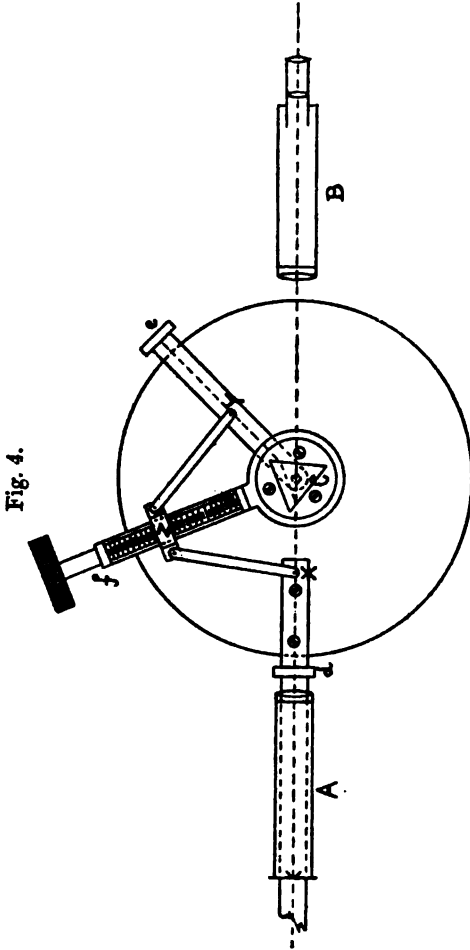
Another form of instrument is illustrated in plan in fig. 4 and in elevation in fig. 5. In this case one prism and two plane mirrors are used.

$A$  is the collimator and  $B$  the telescope.  $C$  is the prism mounted on a levelling-table which rests on and turns with the arm  $Cf$ .  $d$  is a plane mirror fixed above the object-glass of the collimator and facing towards the prism.  $e$  is a plane mirror supported on the extremity of the arm  $Ce$ , and also facing towards the prism. The arm  $Ce$  is free to turn round the centre of the table of the instrument. To the arm  $Cf$  is attached a screw carrying a block  $Z$ , which is free to move along the arm, and is linked to a pin  $X$  fixed on the table of the instrument and to a pin  $Y$  on the arm  $Ce$ . To use the prism with minimum deviation  $ZX$  and  $ZY$  are made equal, and the prism and the mirror  $e$  are moved simultaneously by turning the screw.

The beam of light emerging from the collimator  $A$  passes



under the mirror *d* and is deviated by the prism. The mirror *e* is so placed that the light strikes it near its lower edge and goes back through the prism. The beam being inclined slightly upwards, now strikes the mirror *d*, and so is



reflected backwards and forwards between the mirrors traversing the prism at each journey and gradually climbing upwards until finally it passes from the mirror *d* over the top of the prism into the telescope B. If the prism and mirrors



are once properly adjusted for minimum deviation for light of one refrangibility, they are brought in adjustment into the position for any other refrangibility simply by turning the head of the screw *Cf*.

### III.

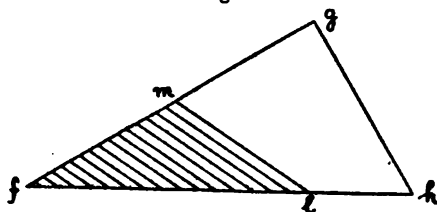
A third form of instrument which may be convenient when it is desired to have the reversed beam in a separate position from the direct one, is shown in plan in fig. 6 and in elevation in fig. 7 (p. 122).

A and B are the collimator and telescope as before. The refracting prisms are *cde* and *fgh*. *k* is a right-angled reflecting prism above the object-glass of the collimator. The beam from the collimator inclined slightly upwards as before is refracted at the face *cd* of one prism, is totally reflected at the face *de*, and emerging at the face *ec* enters the face *hf* of the next prism, is totally reflected at the face *gh*, and refracted out at the face *fg*. The angles and positions of the prisms are made such that the beam emerging from *fg* is parallel to that entering at *cd*, except for a slight inclination upwards. After leaving the two refracting prisms the beam enters *k*, which returns it after two reflexions to the face *cd* in a direction parallel to that in which it first entered that face. Thus the beam circulates round the system of three prisms, gradually rising until it finally passes over the top of the prism *cde* into the telescope B. For adjustment of the refracting prisms they are mounted on levelling-tables which are free to turn about centres at *p* and *q*, and are linked as shown in fig. 6 to a screw working in a fixed block Y, so that by turning the screw the angle between the faces *ce* and *fh* can be altered while the positions of the prisms are kept symmetrical with respect to the central line of the system. Thus when the instrument is adjusted for one wave-length, the whole spectrum can be brought into view by simply turning the adjusting screws.

It is not necessary that the refracting prisms be complete, because a ray entering near *c* strikes the face *ec* after refraction, and is for present purposes lost; consequently the portion shaded in fig. 8 may be cut from the prisms at the corners *c* and *f*. If *hgm* is the actual form of prism used,

it is necessary to cut it so that the beam in passing between the refracting prisms meets the faces  $ce$  and  $fh$  as nearly as possible at normal incidence; because if, for instance, the

Fig. 8.



prism were made triangular of the form  $hmg$ , the refraction at the face  $mh$  would produce dispersion opposite to that due to  $mg$ .

This instrument is much inferior to the others in resolving power. To get the internal reflexions in the refracting prisms total, it is necessary to make the refractions at a large obliquity. That gives, no doubt, considerable dispersion. But the difference between the longest and shortest paths of rays through the refracting prisms is comparatively small. For flint-glass the angles at  $d$  and  $g$  do not differ much from  $90^\circ$ ; so that if  $de = a = gh$  and the angles at  $e$  and  $h$  are about  $60^\circ$ , the difference of the paths for the pair of prisms is about  $\frac{a}{2}$ . Whereas the same two prisms with the corners at  $e$  and  $f$  not cut off, used as reflecting half-prisms in the arrangement first described, would give a difference of path about  $4a$  for rays traversing each once. That is to say, the resolving power of such an instrument of type I. would be about eight times that of one of type III.

Other combinations involving similar principles will readily suggest themselves. But the three described are sufficient to illustrate the method. The number of transmissions may be increased by lengthening the prisms or mirrors. The length of slit that can be used may be increased in the same way. In the instruments I have had made for trial the prisms and mirrors were 5 centimetres high and gave very good results. They are simple in construction, and the adjustments are easy compared with those of a train of prisms. Moreover, by a few

turns of an adjusting-screw one can change the number of transmissions, and with them the degree of dispersion, step by step through a wide range.

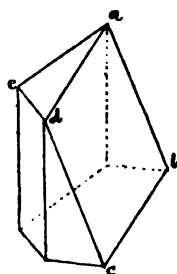
#### IV.

[*Addition made Dec. 6, 1901, after the reading of the paper.*]

Another arrangement in which the reflectors are totally reflecting prisms is shown in figs. 10 and 11 (p. 126).

The back of the half-prism instead of being silvered is formed into a right-angled totally-reflecting prism with its edge at right angles to the refracting edge of the half-prism,

Fig. 9.



as shown in fig. 9. The beam is reflected back to this combined half-prism and reflector by two right-angled prisms  $fh$  and  $lm$ , as shown in figs. 10 and 11. The prism  $fh$  is exactly half the breadth of the refracting prism, and is exactly opposite to the full upper half of it. The prism  $lm$  is of the same size as  $fh$ , but has its lower edge at a lower level than the bottom of the refracting prism, so that a space is left between the reflecting prisms. A beam of light from the collimator passes from  $C$  between the reflecting prisms, is refracted and reflected at the half-prism, and so passes to and fro, taking the course indicated by the arrows in figs. 10 and 11, and finally passes from the reflector  $lm$  under the refracting prism into the observing-telescope at  $T$ . The result in dispersing and resolving power is equivalent to passage through a train of as many complete prisms as there are to-and-fro journeys of the beam.

This arrangement is better than I. and II., because less light is lost by reflexion ; and it is better than III. because it gives full resolving power. Moreover, the beam passes

Fig. 10.

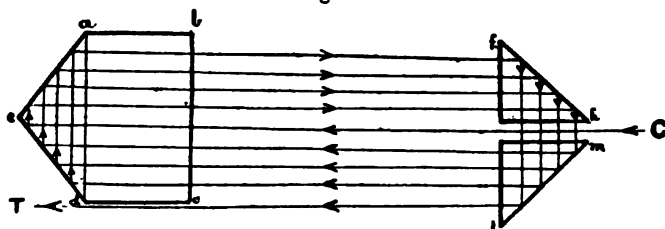
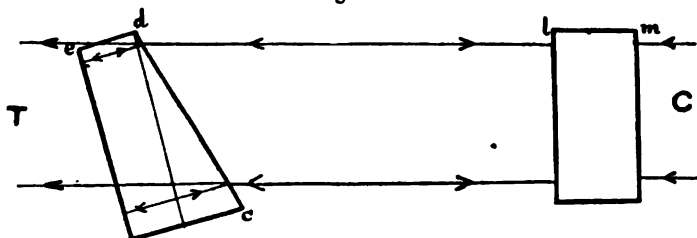


Fig. 11.



through the refracting prism in a principal plane, so that all the prisms may be placed quite close together, and the apparatus thus made more compact. The number of transmissions possible depends upon the width of the opening left between the reflecting prisms  $fh$  and  $lm$ . A very large number of transmissions may be used if this opening is made small. Another possible form would be to make the prisms  $fh$  and  $lm$  also refract, by giving them the form produced by cutting the prism of fig. 9 by a plane through  $e$  at right angles to the face  $abcd$ .

#### DISCUSSION.

Prof. J. PERRY asked if the third form of spectroscope, in which there is total internal reflexion, had been tried experimentally. The amount of light lost at total internal reflexion is much less than at reflexion from mirrors, and he had found that the chief difficulty in using multiple reflexions from mirrors was the great absorption of light.

Dr. R. T. GLAZEBROOK said he would like to know whether the author had any measure of the relative brightness of the first and last spectra.

Mr. W. F. STANLEY said that by using three prisms instead of two it would be possible to substitute, in the first form of spectroscope, total internal reflexion for normal reflexion at a silvered surface.

Prof. THOMPSON suggested a possible way of improving the third arrangement by using two prisms with their apices outwards, refracting at both faces, but not in the position of minimum deviation. Twenty-five years ago the present Astronomer Royal suggested the use of half-prism spectroscopes, and although they are often described in books they are seldom actually used. The advantage of using total internal reflexion is well known, and is exemplified in binoculars, in some of which there are eight reflexions from the object-glass to the eye-piece. He congratulated the author upon the mechanical arrangements used in his spectroscopes.

Prof. CASSIE said that there was no confusion of spectra due to overlapping. With an ordinary Bunsen-burner sodium flame a series of about five spectra are easily observed with dispersion equivalent to direct transmission through ten full-sized prisms. The loss of light at the reflexions limits the number of transmissions that can be used; but he believed that no other spectroscope with only two prisms would give dispersing power and resolving power in any way approaching the instrument described.

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IX. *Air-Pressures used in playing Brass Instruments.* By  
EDWIN H. BARTON, D.Sc., F.R.S.E., Senior Lecturer in  
*Physics at University College, Nottingham*, and S. C. LAWS,  
B.Sc., "1851 Exhibition" Science Research Scholar \*.

[Plates II. & III.]

It is well known that in playing upon the "brass" or "wood-wind" instruments of the orchestra the particular note, at any instant desired, is produced by the simultaneous use of the mechanism of the instrument and the corresponding "embouchure," through which air at a suitable pressure is driven by the performer. The mechanism adjusts the length of the tubing in use so that the note in question is one of those with which the instrument is now in resonance. The correct embouchure and air-pressure pick out, as it were, from the notes then possible to the instrument, the particular one sought, and cause it to sound.

Some of the problems here involved are chiefly of a musical character.

But the pressure of air which solicits the desired note, although several others are possible with the same fingering, and the variations of this pressure with the pitch, loudness, and other circumstances form a problem belonging rather to the domain of physics, and one which is attacked in the experiments here described.

Some previous work on the air-pressures required for various instruments has been done by Dr. W. H. Stone (see p. 171, 'Elementary Lessons on Sound,' Macmillans, 1891), who gives maximum and minimum pressures for the oboe, clarinet, bassoon, horn, cornet, trumpet, euphonium, and bombardon. No details, however, are there given of the pressures for each note of the scale, nor of the variations of the pressure with loudness.

The present work deals with three brass instruments, viz., the tenor trombone, the trumpet, and the cornet. The results of the experiments on these are sufficiently consistent

\* Read December 13, 1901.



to support certain general conclusions which are summarized at the close of the paper.

*Experimental Method.*—Following the hint given by Dr. Stone, the pressures were taken by a water-manometer connected to the performer's mouth by an indiarubber tube terminating in a glass nozzle which could be held by the side teeth. After a little practice, the instrument could be played without the insertion of this side nozzle producing any serious annoyance. The open end of the manometer was provided with a plug of cork and cotton-wool which just damped out the oscillations of the water columns in it without interfering with their prompt assumption of the correct levels when a note was sounded. To arrest the columns immediately in these positions and retain them there until the readings were taken, a pinch-cock was used on the indiarubber pipe connecting the manometer with the player's mouth. Thus the *modus operandi* was as follows:—A series of notes and their loudness being decided upon and indicated in the note-book and the player and recorder in position, the recorder calls for a certain note, at the same time opening the pinch-cock. The player sounds the note and sustains it till it is judged to be of the desired intensity; the pinch-cock is then released, thus immediately closing and so retaining the water columns in place. These are read and recorded and then the next note is called for.

The manometer-scales were graduated to centimetres and estimated to quarters of a division.

A mercury manometer was tried for some of the higher pressures exceeding a metre of water, but was quickly abandoned as being far less convenient.

*Lines of Investigation.*—It was decided to find how the air-pressure required to sound the different notes varied with (1) the pitch of the note, (2) its loudness, (3) the fingering or other manipulation of the instrument, (4) the instrument itself. In each of these cases of inquiry as to the effect of any one variable cause, the other variables were kept constant so far as circumstances permitted. Thus, to test how the pressure depended upon pitch, a scale was played with the loudness maintained as nearly as possible the same. The fingering was, however, necessarily changed to produce the

consecutive notes of the scale. Again, for dependence of pressure on loudness, the same note was played with various intensities, then another note with various intensities, and so on. Thirdly, where the same note was obtainable with two fingerings, the sound was obtained of the given pitch and with the same intensity, first with the usual and then with the alternate fingering.

*The Scale on Brass Instruments.*—In order to render subsequent references quite clear, it seems desirable to explain here how the scale is obtained both with slide and valve instruments. In the slide instruments, when the slide is in the first position, *i. e.* closed, the minimum length of tubing is in use, and the only notes obtainable are those with which that length of tubing is in resonance. These form the harmonic series, the relative frequencies of the notes being 1, 2, 3, 4, 5, 6, &c.; the fundamental or prime is termed by musicians the “pedal” and is rarely used. By drawing the slide out to the second position, sufficient length of tubing is introduced to put the instrument in resonance with notes a semitone lower. The other positions to the seventh inclusive lower the notes of the instrument by a tone, a tone and a half, &c. to three tones respectively. The use of the slide has thus three effects: (1) it furnishes the complete chromatic scale in the largest interval which occurs between the notes in use natural to the instrument with the slide closed, *viz.*, between the second and third harmonics, whose interval is a fifth; (2) and consequently it more than bridges all the other intervals (fourth, major third, &c.) which occur in the higher part of the harmonic series, thus giving alternate methods of playing various notes; (3) it extends the scale downwards.

In valve instruments the same results are usually approximately obtained by the use of three valves. The first valve, when depressed, adds sufficient tubing to lower the notes by a whole tone, the second valve a semitone only, and the third about a tone and a half.

These facts are exhibited collectively in Table I. for an instrument tuned to B $\flat$  like the Cornet and Tenor Trombone. The lower notes are at the bottom of the table. Those in round brackets indicate alternative fingerings. The numerals

under some of the notes give approximate frequencies for the trombone in complete vibrations per second. For the cornet, all these require doubling.

TABLE I.—The Scale on Slide and Valve Instruments.

Positions of Slide on Trombone.	1st.	2nd.	3rd.	4th.	5th.	6th.	7th.
Valves depressed on Cornet.	None.	2nd.	1st.	1st & 2nd.	2nd & 3rd.	1st & 3rd.	1st, 2nd, & 3rd.
Number of partial tone or "Harmonic" elicited by suitable "embouchure" and air-pressure.	Names of Notes.						
8	B $\flat$ 480	A		G			
7	This harmonic is not generally used.						
6	F 360	E		(D) 300			
5	D 300		C		(B $\flat$ ) 240		
4	B $\flat$ 240	A		G		(F) 180	
3	F 180	E		D		C	B
2	B $\flat$ 120	A		G		F	E
1	B $\flat$ 60	This prime note, called the "pedal," is not generally used.					

**EXPERIMENTAL RESULTS.** *Tenor Trombone.*—The instrument used for these experiments is in B $\flat$  by Millereau & Co. of Paris, and was throughout played by E. H. Barton with a Higham mouthpiece.

The mean results of scales and exercises over two octaves tried on it at different intensities are given in Table II., and

graphically exhibited in Plate II. The ordinates of the curves are the manometer pressures in centimetres of water, and the abscissæ represent the intervals in cents, the intonation being assumed in equal temperament.

Both in the table and on the Plate the C in square brackets is the middle C between the staves, and is of frequency about 269 complete vibrations per second.

TABLE II.—Pressures for Scales on Trombone.

Notes .....	F	G	A	B $\flat$	C	D	E	F	G	A	B $\flat$	[C]	D	E	F
Positions of Slide. }	6	4	2	1	6	4	2	1	4	2	1	3	1	2	1
<i>f.</i> Mean of 4 sets. }	18	26	32	37	40	47	53	58	65	73	80	88	108	117	122
<i>m.</i> Mean of 11 sets. }	17	23	27	31	34	42	51	52	57	63·7	64·2	71	76	81	90
<i>p.</i> Mean of 4 sets. }	13	17	22	27	27·5	35	42	39	44	48	45·5	52	59	65	74

The results of experiments on given notes sounded in close succession but with different intensities are given in Table III.

The experiments as to change, if any, of pressure with change of fingering are detailed in Table IV.

*Cornet.*—These experiments were made with a Higham Cornet played by a professional trumpeter and cornettist, Mr. E. C. Pickerill of Nottingham. The results for scales over two octaves soft, medium, and loud, each played once only, are shown by the three curves on Plate III. marked respectively *p*, *m*, and *f*. The C in square brackets denotes the middle C between the staves. The abscissæ and ordinates are as in Plate II.

TABLE III.—Pressures for given Notes, Loud and Soft.

Notes .....	F	B $\flat$	F	B $\flat$	D
Approximate frequencies.	90	120	180	240	300
Positions of Slide.	6	1	1	1	1
<i>pp.</i>	13	24*	27	50	73.5
<i>p.</i>	13	34.5	50	57	83
<i>m.</i>	19.5	36.5†	55.5	63	88.5
<i>f.</i>	23	40	67.5	82	106
Single crescendo notes. }		<i>pp</i> 20 to to <i>f</i> 38 }	<i>p</i> 50 to to <i>ff</i> 78 }	<i>p</i> 61 to to <i>ff</i> 101 }	

\* This pressure was obtained with a small aperture between the lips. With a larger aperture, the note still being *pp*, the pressure fell to 15!

† The pedal note an octave lower than this was produced *m* with a pressure of 7 cm.

TABLE IV.—Pressures for same Notes in Alternative Positions.

Notes .....	F		Bb		D		
Approximate frequencies.	180		240		300		
Positions of Slide.	1	6	1	5	1	4	
No. of "Harmonic" used	3	4	4	5	5	6	
1st Series (1897).	<i>p</i>	50.5	48	72	70	72	67
	<i>mf</i>	50	50	75	75	98	92
	<i>f</i>	73	68	94	92	119	117
	<i>ff</i>	80	83	113	110		
2nd Series (1901)	<i>m</i>	55	50	67.5	68.5	72	72

The experiments on the cornet as to different intensities of given notes are detailed in Table V.

TABLE V.—Pressures for given Notes, Loud and Soft.

Notes .....		A	E	A	C♯	E
Approximate frequencies.		226	339	452	568	678
		Pressures.				
Intensities.	<i>f</i>	26·75	34·25	44	52·75	66
	<i>m</i>	22·5	26	31·5	38·75	41·5
	<i>p</i>	12	15·5	20·5	30·25	34

*Trumpet.*—For the experiments on the Trumpet a Besson trumpet in F was used, played by Mr. E. C. Pickerill with a mouthpiece by H. Keats & Son. The results of once playing the scale in F through two octaves at medium intensity is shown on Plate III. by the dotted curve marked TT.

*Comparison of Trumpet and Cornet.*—Table VI. gives the result of a comparison of trumpet and cornet as to the pressures for given notes of different intensities.

TABLE VI.—Trumpet and Cornet compared.

Notes .....		B♯	F	B♭	D	F
Approximate frequencies.		240	360	480	600	720
Trumpet.	<i>f</i>	25·75	43·75	45·5	48·75	68
	<i>m</i>	23·25	28	34·5	41·5	57·25
	<i>p</i>	16	18·5	26·75	28·75	42
Cornet.	<i>f</i>	26·5	45	47·25	55·75	75·75
	<i>m</i>	18	28·5	32·75	41	51·75
	<i>p</i>	13	21	22·5	32·25	39·25

*Conclusion.*—In reviewing the results of the experiments it is clear that the following general inferences may be drawn:—

1. Other things being equal, the louder the note the greater the pressure, as was to be expected. See Tables III., IV., V., and VI.

2. Again, all else being retained the same, the higher the pitch of the note played on a given instrument the greater the air-pressure used. See Tables III., V., and VI.

In the scales (Table II. and Plates II. & III.) this is sometimes apparently violated, not only on the trombone played by the writer but also in the professional playing of the trumpet and cornet. This seems to be due to a slight unintentional difference in intensity or in the manner of producing the notes. (See first footnote to Table III.) In the higher parts of the scale it is hard to avoid increasing the loudness. This may account for the upward turn of the curves at this part.

3. In the preliminary experiments, on plotting the frequency of the notes of the scale as abscissæ and the pressures as ordinates fairly smooth curves were obtained convex upwards. When, however, quantities proportional to the logarithms of the frequencies are taken for abscissæ, the curves become almost straight lines. See Plates II. & III., in which the abscissæ are Mr. Ellis's logarithmic cents, 100 to the equally-tempered semitone, represented by the large squares, and the intonation is assumed to be in equal temperament.

4. Now if the logarithms of the frequencies be taken to measure pitches of notes, then the difference of logarithms measures the ratios of frequencies, *i. e.* measures the intervals between them. And, as is well known, this is the only way which admits of simple addition of numbers representing the component intervals giving the number representing the resultant interval. Thus the logarithm of the frequency is in a certain very real and important sense the best physical measure of the pitch of a note. Hence, adopting this method, and noting that the curves in Plates II. & III. are nearly straight lines, we may say that the air-pressure required to sound any note with given intensity is approximately proportional to its pitch defined logarithmically.

5. Where alternative positions or fingerings are used for the same note the pressures are practically the same, see Table IV., the results in which were confirmed also by Mr. Pickerill with his instruments. In other words, it is almost indifferent as regards pressure required, whether a note is played on a given instrument as the third harmonic of a short tube or the fourth of a longer one, &c., &c. This is contrary to what is implied by some writers.

6. The pressures for identical notes on trumpet and cornet are almost the same for any given intensity, but very much less than those for the same notes on the trombone. See Table VI. and Plate III. (*cf.* with Table III. and Plate II.).

7. The pressures used for loud low notes may exceed those for soft high notes, in some cases even where the notes are an octave apart. See Tables III., IV., V., and VI., also Pls. II. & III.

8. The present results as to maximum and minimum pressures are in accord with Dr. Stone's, so far as comparison is possible.

Our thanks are due to Mr. Pickerill for kindly placing his services at our disposal.

University College, Nottingham,  
August 1901.

#### DISCUSSION.

Prof. J. D. EVERETT said the paper was an interesting attempt to make a quantitative connexion between theory and practice, and the linear law connecting logarithmic frequencies and pressures came out well from the experiments. He asked if the pressure necessary depended on the skill of the operator.

Mr. D. J. BLAICKLEY said that soon after the publication of Dr. Stone's experiments on this subject he followed up the matter by experiments of his own, using a simple water-pressure gauge. The general results agreed fairly well with those given in the paper, but from them one law appeared to be deducible which was not suggested by Dr. Barton and Mr. Laws, and which greatly modified their conclusion (4). His observations showed that when the intensity was reduced to the lowest possible point for each of the notes in a given



series, the resulting minimum pressures were directly proportional to the frequencies, and not to the frequencies as defined logarithmically. It was further noticed that whether a given note, as say B $\flat$  of 240 vibrations, was sounded as the eighth harmonic of a contrabass, the fourth harmonic of a tenor trombone or euphonium, or as the second harmonic of a cornet, the result was approximately the same. The minimum pressure at which any note can be sounded appeared to depend solely upon its pitch, and not upon the place of the note, upon the instrument used, or upon the calibre or total mass of air in the instrument.

Mr. WATSON suggested that if different gases were used to blow the instruments, the results might depend upon the velocity of sound in the gas used.

### X. *A new Hygrometric Method.*

By E. B. H. WADE, M.A.\*

(1) *THE object of this note* is to describe a new hygrometric method, in which a thermometer is wetted not with water but with sulphuric acid of suitable strength.

(2) *It is claimed* that the method is (a) theoretically sound, (b) cheap and easy to manipulate, (c) specially suited for the study of ordinary wet bulbs, (d) independent of ventilation.

(3) *Theory of the method.*—Let  $t$  = temperature of dry bulb,  $t'$  = the same for wet bulb,  $\theta$  = the same for bulb wet with acid (acid bulb);  $f$  = tension of vapour in air,  $f'$  = maximum tension of water-vapour at  $t'$ ,  $\phi$  = maximum tension for acid at  $\theta$ . If  $t = \theta$ ,  $f = \phi$ , and  $\phi$  is known from Regnault's work. Hence  $f$  follows. In studying wet bulbs by this method assume further that over a small range of conditions

$$f = f' - c(t - t') = \phi - k(t - \theta),$$

and from two such comparisons obtain  $c$  and  $k$ , or from a large number treated by the method of least squares.

\* Read December 13, 1901. Published by permission of the Under Secretary of State, Public Works Ministry.

The range of conditions over which it is admissible to assume that  $c$  and  $k$  are constant must be found by experiment, but it must be admissible over some range. Special attention is drawn to this device for finding  $c$  and  $k$ , since it does not involve an appeal to any method supposed to be standard.

(4) *Manipulation*.—To apply this theory to the study of wet bulbs, the bulb of a thermometer is wrapped in linen secured by a rubber band just above the bulb. A little higher the stem passes through a rubber stopper, which closes the mouth of a test-tube containing a little acid which wets the rag. When this thermometer reads about the same as the dry bulb, withdraw the test-tube exposing the rag to air. Between the fourth and sixth minutes after this, read repeatedly the acid thermometer and the wet and dry bulbs, and take the respective means. Rinse the linen repeatedly with the stock of acid and replace the test-tube. A very little experience enables one (from a reading of the wet and dry bulbs at 8 A.M.) to select a solution which will be appropriate to the humidities met with during most of the morning and again in the evening. A point is made of the simplicity of the method.

(5) *Illustrative results*.—The results below are to illustrate the method and to show that  $k$  may be taken constant between limits  $t - \theta = \pm 2^\circ$  and in very different ventilations. Table I. gives results with the apparatus described and an ordinary psychrometer. Light winds prevailed, but an exact record was not kept. The series is preliminary:  $k$  appears constant, but the question of ventilation remains. To test this the ordinary psychrometer was replaced by Assmann's well-known construction. The high artificial ventilation of this instrument is thought to render it independent of changes in the natural ventilation. The acid bulb was still exposed to the natural ventilation which was estimated on a scale whose unit is about 6 kilometres per hour. The agreement of columns  $f_1$   $f_2$  in Table II. is held to show the acid bulb's independence of ventilation.  $k$  is practically the same as in Table I. over range  $t - \theta = \pm 2^\circ$ . The value of  $c$  was taken as unknown.



D.	W.	A.	$f_1$ .	$f_2$ .	Diff.	Acid.	V.
20.0	15.2	21.4	10.9	10.4	+0.4	A	4-5
20.0	15.7	22.0	11.6	11.5	+0.1	A	0
20.9	15.2	21.9	10.5	10.5	0.0	A	0
22.5	16.7	23.8	11.8	11.9	-0.1	A	5
21.9	15.9	22.6	11.0	10.7	+0.3	A	4
22.2	16.1	22.9	11.2	10.9	+0.3	A	3
22.7	16.4	23.3	11.4	11.0	+0.4	A	4
22.6	16.2	25.6	11.1	11.0	+0.1	B	0
21.6	14.8	21.6	9.8	9.4	+0.4	A	0
23.9	17.0	24.1	11.6	11.1	+0.5	A	4
22.9	16.0	23.2	10.7	10.6	+0.1	A	3
27.1	20.2	28.2	14.8	15.0	-0.2	A	3
26.3	19.4	27.2	13.9	14.2	-0.3	A	2
21.3	14.3	21.3	9.3	9.2	+0.1	A	3
23.5	16.5	23.8	11.1	11.0	+0.1	A	2
24.0	16.8	24.1	11.3	11.0	+0.3	A	3
21.7	14.4	21.4	9.3	9.0	+0.3	A	0
21.2	14.0	23.3	9.0	9.2	-0.2	B	0
21.4	13.8	23.2	8.7	8.8	-0.2	B	2
27.0	19.4	27.6	13.7	13.7	0.0	A	5
23.2	15.6	25.3	10.2	10.2	0.0	B	2
24.9	17.1	27.6	11.4	11.7	-0.3	B	1
23.6	15.9	23.2	10.3	9.9	+0.4	A	4
27.2	19.2	27.2	13.3	13.2	+0.1	A	4
24.0	15.9	26.2	10.2	10.5	-0.3	B	2
22.7	14.6	22.0	9.2	8.9	+0.3	A	2-4
24.9	16.3	23.9	10.2	9.8	+0.4	A	0
22.1	13.3	22.9	7.9	7.7	+0.2	B	3
25.5	16.7	27.5	10.6	11.1	-0.5	B	2
25.9	17.0	27.5	10.8	10.7	+0.1	A	1
27.2	18.2	26.3	11.9	11.7	+0.2	A	5
24.5	15.4	23.3	9.4	9.3	+0.1	A	0
23.4	14.3	22.2	8.5	8.8	-0.3	A	0
23.3	14.0	21.6	8.2	7.8	+0.4	A	0
23.0	13.7	21.4	8.0	7.7	+0.3	A	2
26.4	17.1	28.2	10.8	11.3	-0.5	B	1
25.4	16.0	24.0	9.7	9.6	+0.1	A	2
26.1	16.5	27.2	10.1	10.2	-0.1	B	2
23.3	13.7	21.5	7.9	7.6	+0.3	A	3
25.3	15.6	26.3	9.3	9.4	-0.1	B	1
25.6	15.9	23.8	9.5	9.1	+0.4	A	0
25.5	15.7	23.8	9.4	9.1	+0.3	A	1
23.6	13.6	21.7	7.6	7.6	0.0	A	1
24.6	14.3	22.2	8.0	7.5	+0.5	A	2
26.1	15.6	26.7	9.0	9.4	-0.4	B	2
27.3	16.5	27.7	9.7	9.7	0.0	A	2
25.0	14.1	22.2	7.6	7.1	+0.5	A	4
25.0	14.1	22.2	7.6	7.1	+0.5	A	0
24.4	13.4	24.2	7.0	7.4	-0.4	A	0
26.9	15.8	27.2	8.9	9.3	-0.4	A	3
27.1	15.7	27.1	8.7	9.0	-0.3	A	3
25.5	14.3	22.8	7.6	7.6	0.0	B	2
25.7	14.3	23.2	7.5	8.0	-0.5	A	0
26.6	14.6	23.2	7.6	7.1	+0.5	A	3
27.1	14.9	24.0	7.7	8.0	-0.3	A	2
26.3	14.2	25.2	7.2	7.0	+0.2	B	4
28.4	16.2	26.1	8.8	9.2	-0.4	B	2
25.9	13.3	24.8	6.4	6.8	-0.4	B	4
19.3	16.5	26.1	8.8	8.4	+0.4	A	0
25.4	12.5	24.0	5.7	6.1	-0.4	A	3
24.8	11.8	23.2	5.1	5.6	-0.5	A	1
29.1	16.1	28.2	8.4	8.8	-0.4	A	3

Table III. deals further with ventilation. A wet bulb and an acid bulb were mounted at opposite ends of a diameter of a whirling machine, in a room where the air was very calm and of even temperature. They were read at rest and again after 2 minutes' whirling at about 6 metres per sec. The result shows an almost perfect immunity towards ventilation except in the cases where  $D - A$  exceeds  $\pm 3^\circ$  (see Table III.). The observers who kindly assisted were kept entirely unaware of the effect to be looked for.

TABLE III.

$D$  = Temperature by dry bulb thermometer.

$W_1 =$	"	wet	"	before	} whirling.
$W_2 =$	"	"	"	after	
$A_1 =$	"	acid	"	before	} whirling.
$A_2 =$	"	"	"	after	

All bulbs 0.9 centimetre diameter.

Strengths of acid adjusted to give very different values of  $D - A$  for similar values of  $D - W$ .

D.	$W_1$ .	$W_2$ .	$A_1$ .	$A_2$ .	$D - A_1$ .	$A_1 - A_2$ .	$W_1 - W_2$ .	Observer
24.0	15.8	15.0	20.7	20.6	3.3	+0.1	+0.8	M.K.
23.8	15.8	14.8	21.2	21.0	2.6	+0.2	+1.0	"
23.8	16.0	15.3	18.6	18.2	5.2	+0.4	+0.7	"
23.8	15.8	15.0	22.8	22.6	1.0	0	+0.8	"
23.7	16.1	15.3	23.7	23.8	0	-0.1	+0.8	"
23.8	16.2	15.3	26.2	26.1	2.6	+0.1	+0.9	"
23.7	16.2	15.3	29.6	29.2	5.0	+0.4	+0.9	"
23.6	16.0	15.3	27.5	28.0	-3.9	-0.5	+0.7	"
24.4	16.2	15.4	27.0	27.2	-2.6	-0.2	+0.8	"
28.6	15.8	15.0	27.6	27.6	-4.0	0	+0.8	W.
23.6	15.8	15.0	27.2	27.3	-2.6	-0.1	+0.8	"
23.4	16.0	15.2	26.0	26.0	-2.6	0	+0.8	"
23.4	15.6	14.8	25.4	25.6	-2.0	-0.2	+0.8	"
23.4	15.8	15.0	25.2	25.4	-1.8	-0.2	+0.8	"
23.4	15.6	14.6	25.2	25.2	-2.2	0	+1.0	"
23.4	15.8	15.0	24.8	24.9	-1.4	-0.1	+0.8	"
23.2	15.8	15.1	24.4	24.6	-1.2	-0.2	+0.7	"
23.0	16.0	14.6	24.4	24.5	-1.4	-0.1	+1.2	"
23.4	15.7	14.8	24.4	24.4	-1.0	0	+0.9	M.S.
21.4	15.6	15.1	20.6	20.6	+0.8	0	+0.5	W.
22.2	15.0	14.4	19.0	19.0	+3.2	0	+0.6	"
22.2	14.9	14.2	19.9	19.9	+2.3	0	+0.7	M.K.
22.6	15.4	14.8	20.8	20.8	+1.8	0	+0.6	"
22.8	15.6	14.9	18.5	18.1	+4.3	+0.4	+0.7	"

(6) *Applicability of the method.*—The method is recommended as a reference method to those who wish to find the constants for their wet and dry bulb. They may proceed

exactly as described above, preferably taking  $c$  and  $k$  as both unknown. The method is also available as a substitute for the wet bulb. It cannot compete in simplicity with the wet bulb in its simplest form, but it can compete with the various modifications (whirled thermometers, &c.).

For the range studied the constant  $\cdot 93$  can be used for  $k$ , and it is hoped that this will be tested for other climates and below the freezing-point. A small error in  $k$  is of very little importance, owing to the small value of  $t - \theta$ .

(7) *Conclusion.*—The method has been shown simple; the elementary theory is thought rigorous; the extension to small thermal effects is justified in numerous experiments;  $k$  has turned out to be very nearly  $\cdot 93$  over as wide a range as was open to study;  $c$  is unexpectedly low. The last point requires some discussion. According to a mass of published dew-point observations, a value  $0\cdot 5$  for  $c$  was expected in Table II., and the writer thinks it superfluous to make additional dew-point observations. The low value  $0\cdot 4$  found for  $c$ , though opposed somewhat to the dew-point results, is favoured by Maxwell's theory\*. To make  $c = \cdot 5$  in high ventilation is to make his ratio  $\frac{K}{D}$  (*loc. cit.*) practically unity, but he considers it probably  $\cdot 77$  and "certainly less than unity." His estimate is supported by the experiments of Graetz, Winkelmann, and of Kundt and Warburg, so that a considerably lower value of  $c$  is suggested. *It is not, however, the object of this note to determine the value of  $c$ .* It is the method with its theoretical and practical claims which is put forward. A wider basis was rendered impossible from want of leisure.

Abbasia Observatory, Egypt.

August 22, 1901,

#### DISCUSSION.

Prof. J. D. EVERETT criticised the paper at length, and said he could not commend the method described.

Prof. A. S. HERSCHEL said that to free the proposed mode of observation from any objections which could be raised to it on the score of defective theory, tables might, perhaps, be

\* Art. "Diffusion," *Encyc. Britt.*

constructed for use with the author's instrument, similar to the one constructed long ago by Mr. Glaisher, and now still generally used by meteorologists, to find the dew-point temperature from readings of the ordinary wet and dry bulb hygrometer.

Mr. W. WATSON replied to some of Prof. Everett's remarks, and pointed out some of the advantages of the method described in the paper.

### XI. *On Focal Lines, and Anchor-Ring Wave-Fronts.*

*By* Prof. J. D. EVERETT, F.R.S.\*

WHEN a small cone of rays is obliquely incident on a spherical reflecting or refracting surface, the rays after reflection or refraction no longer compose a true cone. Instead of meeting in a point they form a narrow neck; and this neck is flattened in two places called the primary and secondary foci, the planes of flattening being at right angles to each other. Optical writers give the name *focal lines* to the sections of the pencil made at these two places by planes perpendicular to the axis of the pencil; but it would be more appropriate to give the name to the sections which most nearly resemble lines, whatever angle they may make with the axis of the pencil.

Clearness of conception, in intricate matters, is greatly aided by sharply defined illustration; and I wish to call attention to a case (which appears to have been hitherto overlooked) in which all the rays, even of a large pencil, pass accurately through two definite lines: one of these lines being a circular arc cutting the pencil at right angles; and the other being a straight line, which may have any inclination to the axis of the pencil.

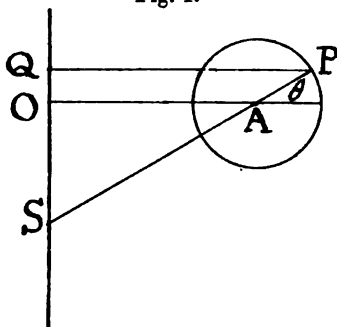
The case is that in which the wave-front in one of its positions is a *tore* (or anchor-ring).

A *tore* may be defined as the surface generated by the revolution of a circle round a fixed straight line in its plane; this line we shall refer to as the *axis of revolution*. A *tore*

\* Read February 28, 1902.

has also what may be called a *circular axis*—the circle generated by the motion of the centre of the revolving circle. In the figure QOS is the axis of revolution, O the centre of

Fig. 1.



the tore, and OA the radius of the circular axis. P is any point on the revolving circle, PQ a perpendicular on the axis of revolution, and  $\theta$  the inclination of the straight line PAS to PQ or AO.

The two focal lines are always at the centres of curvature of two mutually rectangular normal sections of the wave-front, one being the section of greatest and the other of least radius of curvature. For an element of the wave-front at P one of these sections is the circle shown in our diagram, and PA is its radius of curvature. The other is the section of the tore made by a plane through PAS perpendicular to the plane of the diagram. To find its radius of curvature note that QP is the radius of a circular section made by a plane perpendicular to the axis QS; hence, by Meunier's theorem, the required radius of curvature is  $PQ \sec \theta$ , that is PS. The two focal lines are accordingly at A and S. A is called the *primary*, and S the *secondary* focus. If we make P travel round the circle shown in the figure the primary focus remains fixed at A, and the secondary focus travels along the axis QS, its distance from O being  $OA \sec \theta$ , which runs from zero to infinity in both directions. On the other hand, if we make P revolve round the axis QS the secondary focus remains fixed at S, and the primary focus generates the circular axis of the tore.

For a circular element of the wave-front, of small diameter



$d$ , having  $P$  for its centre, the primary focal line will be an arc of the circular axis, of length  $\frac{SA}{SP} d$ ; and the secondary focal line will be a portion of the axis of revolution, of length  $\frac{AS}{AP} d \cdot \sec \theta$ . If, instead of regarding this absolutely sharp line as the focal line, we follow the usual convention, and adopt, as the secondary line, the section of the pencil by a plane at  $S$  perpendicular to  $PS$ , its two ends will be blurred, so that it will resemble a figure of 8, and its length will be  $\frac{AS}{AP} d$ .

At any point  $T$  between  $A$  and  $S$  the breadth of the pencil in the plane of the diagram is  $\frac{AT}{AP} d$ , and its breadth perpendicular to the plane of the diagram is  $\frac{ST}{SP} d$ . The ratio of the latter breadth to the former is  $\frac{ST}{AT}$  multiplied by the constant  $\frac{AP}{SP}$ , and is unity when  $SA$  is divided internally and externally in the same ratio.

Toric wave-fronts can be produced by constructing a concave reflector, of the form generated by making an ellipse, or any portion of an ellipse, revolve through any convenient angle round an ordinate erected at one focus  $O$  of the ellipse; and employing it to reflect rays diverging from a small source of light at this focus. The length of path is the same for all once-reflected rays from  $O$  to the circle traced by the other focus  $A$ , and will, therefore, be the same for all such rays from  $O$  to a tore having this circular axis.

Figs. 2, 3, 4 represent an experimental illustration. Fig. 2 contains an axial section of a reflecting surface of revolution; the section being made up of portions of two equal ellipses of eccentricity  $\frac{1}{2}$ .  $O$  and  $A, A'$  are points corresponding to  $O$  and  $A$  in fig. 1. A point source at  $O$  is provided by means of an opaque disk pierced with a small hole at  $O$ ; the disk being carried by an axis in its own plane, coinciding with a diameter of the bounding circle of the reflector, as shown in figs. 3, 4 (p. 146), which represent the reflector supported on a stand, with its bounding plane vertical, the axis of rotation of the disk being also vertical. By rotation round this axis the

disk can be made to face a source of light at its own level, at any obliquity to the bounding plane. In fig. 2 a beam is shown

Fig. 2.

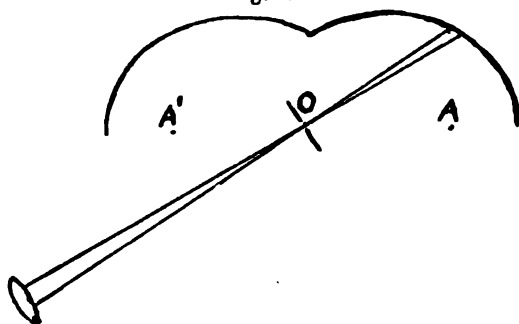


Fig. 3

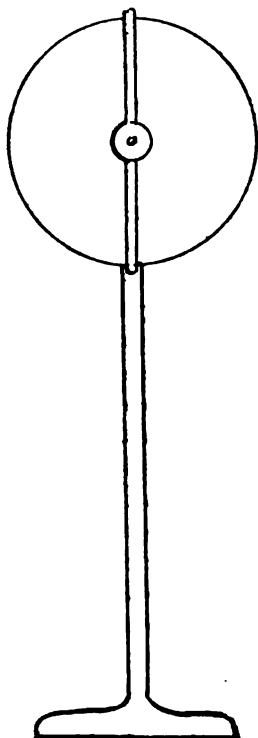
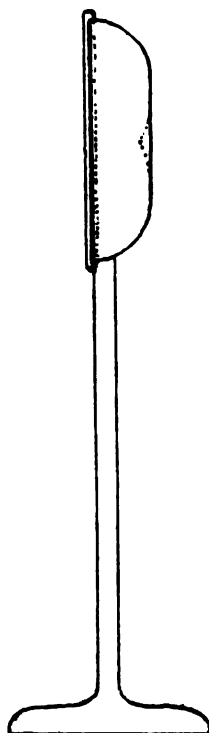


Fig. 4.



focussed on the hole by a lens. The beam may be furnished by a lantern, or by a bright lamp-flame properly screened.

Widening the angle of the pencil given by the lens lengthens and at the same time brightens the focal lines.

The primary line will be a circle having  $AA'$  for diameter, and will be always real. The secondary line will coincide with the axis of revolution, and will be real or virtual according to the position of the area of incidence. For incidence at the extremity of the ordinate through  $A$ , the reflected ray is parallel to the axis, and the secondary line goes off to infinity. Both lines when real can be shown on a translucent screen. The secondary line, when virtual, can be seen by looking into the reflector. The complete circle of the primary can be obtained at once by making the axis of the incident beam (of wide angle) coincide with the axis of the reflector, so that the area of incidence surrounds the central boss.

An iris diaphragm (as used by microscopists) might with advantage be substituted for the pierced disk.

*Postscript.*—Since reading the paper I have found that Maxwell, in a paper entitled "On the Cyclide," has investigated the general form of the wave-surface "when one or both of the so-called focal lines is really a line," and has indicated the anchor-ring as a particular case ('Collected Papers,' vol. ii. pp. 144 & 151).

#### DISCUSSION.

Mr. R. J. SOWTER pointed out that when a thin oblique pencil, or small cone of rays, is reflected or refracted by a spherical surface, the pencil rays form a narrow neck, and that this neck is flattened in two places called the *focal lines* and not the *focal points*, and that the focal lines cut the principal ray or axis of the pencil in the focal points. In the case of thin pencils, the focal lines are elementary and may be considered as straight lines, and an infinite number of planes can pass through or contain them. This leads to the mutually rectangular primary and secondary planes of the pencil being selected. But if the elementary focal line is considered curved, as it is in general, only one containing plane can be chosen, namely, the plane of the curve. Real or physical focal lines are not in planes related with the focal

points as suggested by Prof. Everett. It was also pointed out that the criterion for anchor-ring or toric waves is that the focal lines are respectively a circle and a straight line perpendicular to the plane of the circle and lying in its axis, and that a toric wave-front could be formed by the refraction of a hollow cone of light at an annular ring on a spherical surface. The wave-front in the refracting medium is then toric, that is, it is a circular trough which is part of an anchor-ring. The primary focal line is a circle, and the secondary a straight line of limited length.

Prof. S. P. THOMPSON said that optical writers often used the term focal lines to denote the sections of the wave-surface made by two mutually perpendicular planes through the focal points.

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XII. *The Absorption, Dispersion, and Surface-Colour of Selenium.* By R. W. WOOD, *Professor of Experimental Physics in the Johns Hopkins University* \*.

THE dispersion curves of substances with absorption-bands lying wholly within the visible or infra-red spectrum have been carefully examined within the past few years, in connexion with the modern theory of dispersion. To the best of my knowledge little or nothing has been done with substances in which the absorption begins in the visible spectrum and extends into the remote ultra-violet. Of these media amorphous selenium is a type, strong absorption beginning not far from the D lines, and increasing continuously with decreasing wave-length until, in the ultra-violet, the extinction coefficient has as high a value as in the case of metals. Another substance which I have found worthy of investigation is nitroso-dimethyl-aniline. This substance is most remarkable in its behaviour. It crystallizes in green laminæ which melt at 85 degrees and can be formed into fluid prisms between glass plates. These prisms must be kept fluid by an air-bath, as on solidification they become

\* Read February 28, 1902.

opaque. A prism of four or five degrees gives a most astonishing dispersion when an incandescent lamp is viewed through it. It is quite transparent up to the greenish-blue, and gives a spectrum *twelve times as long as a quartz prism of equal angle*. Pressed into a thin film, it seems to be nearly as transparent as glass of a very pale canary-yellow colour; but if the transmitted light be examined with a spectroscope, the blue and violet end of the spectrum is cut off almost as sharply as if by an opaque screen in the eyepiece. This indicates an exceedingly steep extinction curve; and the course of the dispersion curve within this region will prove most interesting. I am at the present time engaged on the investigation of the absorption and dispersion of this substance, and further discussion will be postponed for the present.

Selenium I have already investigated with the assistance of Mr. A. H. Pfund, one of my students at the University of Wisconsin, to whom I am indebted for a large amount of very faithful work.

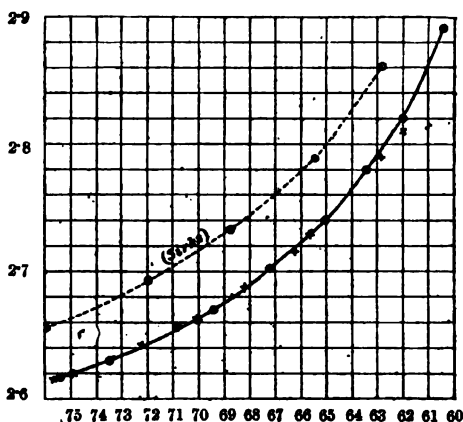
The only determinations that I have been able to find of the dispersion of this substance were made by Sirks\* by the method of the colours of thin plates; a method involving considerable error, as is apparent from a comparison of his curve with the curve obtained by direct spectrometer measurements with selenium prisms.

These prisms were made in the same manner as the cyanine prisms which I have previously described (Proc. Phys. Soc. vol. xvii. p. 671). The substance is much more transparent than cyanine, and larger angles can consequently be used. Four or five degrees is about the maximum angle which can be employed to advantage. A strip of thin German plate-glass about 1 cm. wide and 2 cm. long is about right. A narrow strip of cardboard 1.5 mm. thick is pasted along the narrow edge, and a small piece of selenium fused on the opposite edge by holding the plate over a small flame. The other plate must be heated at the same time to about the same temperature, and the two clamped in a small vice in the manner described for cyanine prisms. It is necessary to

\* Sirks, Dispersion des Selens, Pogg. Ann. cxliii. p. 429.

heat the plate until the substance is quite fluid, which is considerably above the temperature at which it becomes pasty. After the medium has solidified, one of the plates can be removed by a blow from a small hammer, if the prism is required for measurements with the spectrometer, as the angle can then be easily determined by the reflexion of light from the oblique surfaces. If the prism is to be used for demonstration only, it is better to leave the plate on. One of the prisms crossed with a diffraction-grating shows the dispersion curve very well when an arc-light is viewed through the combination.

Determinations were made of the dispersion by means of three selected prisms, the results of which are shown below.



The results obtained by Sirks are plotted for comparison. The values obtained with the different prisms agree very well except at the edge of the absorption-band, where the chance of error is much greater owing to the broadening of the image of the spectrometer-slit by diffraction, the light only passing through a very narrow strip of the prism bordering the refracting edge.

The spectrometer was illuminated with monochromatic light obtained by prismatic analysis, the wave-length being determined for each observation with a glass grating of 14,000 lines. I found it quite impossible to construct prisms of small enough angle to make determinations below wave-length 61

possible. With one very acute prism I fancied that I detected evidences of a decrease of refractive index after passing this point, and accordingly determined to follow the curve further down into the spectrum by means of the interferometer, in the same manner as has already been done in the case of cyanine.

Beautifully uniform films of selenium were obtained on plates of plane parallel glass, by means of a flat selenium cathode in a high vacuum. This cathode was made by rubbing a stick of selenium over a hot aluminium plate, the device being that used by Longden in obtaining films showing Newton's rings.

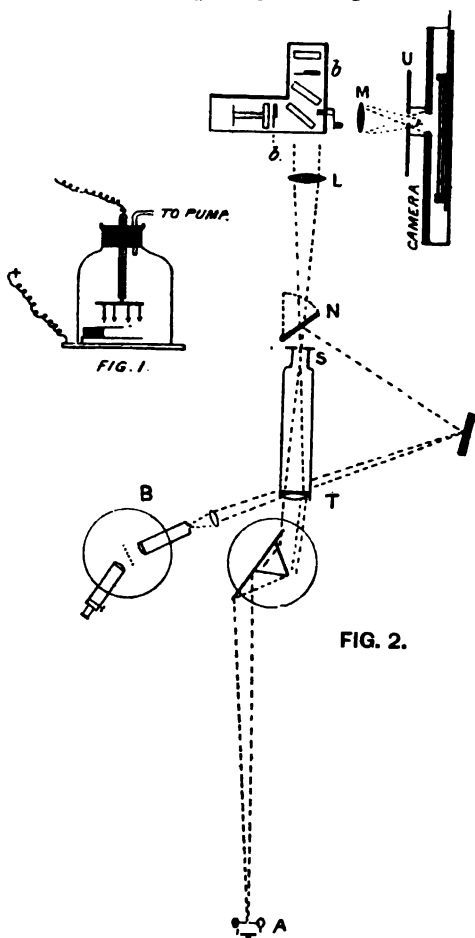
Displacements of the interferometer fringes by the films were obtained in the manner described in previous papers on the dispersion of cyanine and carbon; a film covering one half of each of the two interferometer paths giving double the displacement of a single film without any increased loss of light. The displaced fringes were photographed by monochromatic light of known wave-length, the photographs being subsequently measured with a filar micrometer.

In the photographic work some trouble was had with superfluous light which, being superposed on the image of the fringe system, lessened the contrast between the maxima and minima. Some of this light comes from the glass surfaces and some from the selenium films. Mr. Pfund finally got rid of this light by the ingenious device of placing a convex lens between the interferometer and the photographic plate, which brought the light to two point-foci less than a millimetre apart. A screen with a pin-hole held back the superfluous light, which was collected at one focus, allowing the light which formed the fringes to pass. It was also found that better results were obtained with unsilvered interferometer-plates.

When working in the red and orange comparatively thick films could be used, but in the blue and violet only exceedingly thin ones allowed any light to pass through.

The apparatus as arranged for photographing the fringes and measuring the wave-length of the monochromatic light employed, is shown in fig. 2. The light of an arc-lamp *A* falls on a mirror cemented to the back of a prism which stands on a

revolving graduated circle. The collimator objective T projects a spectrum on the slit S, which can be shifted by turning the circle which carries the prism. The monochromatic light which leaves the slit, after passage through a collimating-lens



L, falls on the interferometer. Plane parallel plates carrying the selenium films are shown at *b*. To get rid of the multiple images, the lens M is arranged so as to focus the light on the perforated screen U\*.

\* By an error of the engraver the aperture in U is shown much too large. Only one of the two convergent beams passes through it.



No other lens is used, the light falling directly on the photographic plate after passage through the pin-hole.

The camera is simply a long narrow box, the plate being carried on a slide, so that eight exposures can be made one after the other on a single plate, measuring  $12 \times 2$  cms.

A small mirror N, hinged in front of the slit, enables us to divert the light from the interferometer and throw it into the grating spectrometer S, by means of which the wave-length can be at once determined. By means of this arrangement it was possible to work with considerable rapidity. After each exposure, the small mirror was turned in front of the slit, and the cross-hairs of the spectrometer set on the diffracted image. The prism was then turned through a small angle and a second exposure given, the circle of the spectrometer being read while the exposure was in progress. The longest exposures in the red were only five or six minutes in duration.

After making a number of measurements in different parts of the spectrum by means of films of different thicknesses, it occurred to me that if a wedge-shaped film were employed, curved fringes would be obtained which would allow the displacement for any wave-length to be measured for the maximum thickness capable of transmitting the light. Films of this nature were obtained by shielding the plate during the deposition with a strip of mica mounted a centimetre or so above its surface, as shown in fig. 1. The drift of the

Fig. 3.



selenium under this shield was very regular, and excellent wedges were obtained which showed straight interference-bands when viewed in reflected light. A series of photographs obtained with one of these prismatic deposits is reproduced in fig. 3. It will be seen from the nature of the displacement of the fringes that the film is of nearly uniform thickness

for a short distance, and then becomes wedge-shaped, the fringes plunging down suddenly.

Another advantage of the wedge-shaped films is that the displaced fringe can be identified with the undisplaced. In working with films in the red and orange, where the displacement is equal to the width of several fringes, the only method of identifying the fringes is to make visual observations with white light at the centre of the system. With the wedge-shaped film there is no difficulty in telling which fringes belong together, for the same fringe can be traced clear across the plate, and the total displacement determined. The chance of making an error of an entire fringe-width in estimating the displacement by visual observations with white light is very great, owing to the great dissimilarity in the appearance of the chromatic fringes seen through clear glass and selenium.

The photographs of the curved fringes were measured by placing them in contact with a glass plate ruled with parallel diamond scratches, one of the scratches being placed in coincidence with the line marking the thin edge of the film. The displacement was measured as before with a filar micrometer, setting the cross-hair first on the undisplaced fringe, and then on the point at which the corresponding fringe intersected the scratch nearest the end of the oblique system.

The values for the refractive indices obtained in the red by means of the prisms were taken as a basis for the calculation of the indices in the rest of the spectrum from the interferometer measurements. If we find the displacement for wave-length  $\lambda_r$  to be  $n_r$  ( $n$  being measured in terms of fringe-width), and know the ref. index  $\mu_r$  for this wave-length, we can determine the refractive index  $\mu_g$  for wave-length  $\lambda_g$  (in the green) by measuring the displacement  $n_g$  for the same thickness, from the formula

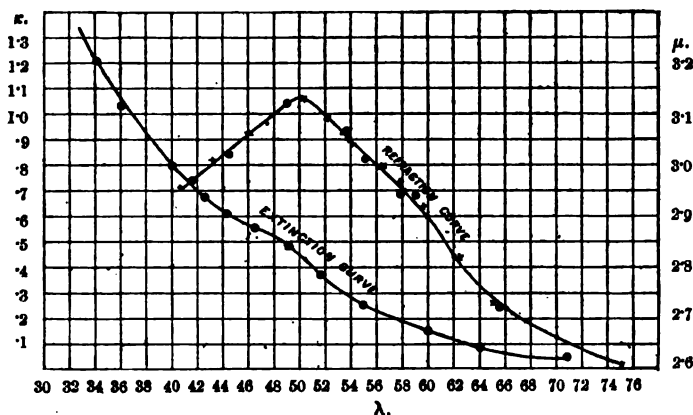
$$\mu_g = 1 + (\mu_r - 1) \frac{n_g \lambda_g}{n_r \lambda_r}.$$

Determinations were made in this way down to wave-length  $\cdot 0004$ , beyond which point it was impossible to go owing to the powerful absorption, which made the fringes too faint to measure. It was only by employing exceedingly thin films

and making the measurements with the greatest care that consistent results were obtained in the violet. The reason for this will be apparent when the subject of absorption is taken up, for a film which in red light is so transparent that its presence cannot be detected, in the violet and ultra-violet absorbs nearly as strongly as a metal film of the same thickness.

The dispersion-curve obtained by means of the interferometer is given on fig. 4, points determined with uniform films being indicated by circles, while points determined with wedge-shaped films are denoted by crosses. The turning point of the curve is at wave-length  $\cdot 0005$ , where the refractive index reaches the value  $3\cdot13$ , which, so far as I know, is the highest value ever found for any substance.

Fig. 4.



The continued rise of the dispersion-curve after entrance into the region of the absorption-band is worthy of notice, for usually the curve falls abruptly as soon as the band is entered. As the matter is of considerable theoretical importance it seemed best to check, if possible, the data furnished by the interferometer by means of very acute prisms. Examination of the wedge-shaped plate by means of sodium light, showed that a strip about 8 mm. wide was suitable for the purpose, the interference-fringes being straight, parallel, and equidistant. The angle was found from the fringes to be very nearly 22 seconds.

The deviations were observed by means of a large spectrometer, which I have recently set up for quantitative measurements of the dispersion of sodium vapour. The slit is illuminated by means of the monochromatic illuminator made by Fuess. The telescope has a focal length of 1.5 metres, the eyepiece being furnished with a filar micrometer. The graduated screw of the monochromatic illuminator, by means of which the wave-length of the light on the slit is changed, is operated from the eye-end of the telescope by means of a long steel rod, while the graduations are read by means of the finder of the telescope, which points towards a mirror in which a portion of the illuminator is seen reflected.

This arrangement is extremely convenient, for the observer can run rapidly through a series of observations without leaving his seat at the eyepiece, a matter of great importance when working with sodium prisms. The plane parallel glass plate with the selenium wedge was covered by a piece of black paper furnished with two apertures, one exposing the prism, the other a portion of the clear glass. The illuminator was set for red light, and the prism placed in front of the telescope: a small screen enabled either aperture to be covered. The image of the slit was slightly broadened by diffraction, but not enough to interfere with accurate setting of the cross-hairs. On changing from clear glass to the selenium wedge, a displacement equal to three times the width of the band was observed. If both apertures were opened simultaneously, both the direct and displaced images appeared in the field, the images being furrowed, however, by the fine interference minima due to two apertures. Though it is quite possible that these minima would furnish the means of a more accurate setting of the cross-hairs on the centre of the band, they were not made use of in the present case, the apertures being uncovered in succession. This seemed advisable in view of the uncertainty regarding the effect of the change of wave-length on their location, for it must be remembered that when working with the strongly absorbed blue light, the amplitude falls off rapidly across the selenium-covered aperture, its effective width contracting with decrease of wave-length. The angular deviation for the

red was measured, and found to agree fairly well with the observations made with prisms of larger angle. The selenium aperture being exposed, the cross-hair was set on the displaced image and the wave-length decreased. The image immediately moved off the hair, which was made to follow it, and a continued increase in the deviation was noted as far down the spectrum as wave-length  $\cdot 00055$ , beyond which point the image became too faint to observe.

I was disappointed not to be able to follow the curve to its turning point in the blue, and accordingly tried another method.

The wedge-shaped film was observed by the light of lithium, sodium, and thallium flames in succession, and the positions of the dark bands recorded by needle scratches. The eighth band for lithium light coincided with the tenth band for sodium light, which agrees well with the observed values of the refractive index. With thallium light only three bands next to the thin edge could be seen, owing to the strong absorption, but their position indicated an increase of refractive index, the third thallium dark band coinciding with the second lithium band. The first dark band moved nearer to the thin edge with decreasing wave-length. A screen consisting of a glass cell filled with a solution of cuprammonium and a sheet of dense cobalt glass was now placed in front of a Welsbach light. This gave a deep blue light free from red. In this case the first dark band was the only one that appeared, but it was distinctly nearer the edge than in the case of the thallium light, which shows that the wave-length of the blue light in the selenium is considerably less than the wave-length of the thallium light, which would not be the case if the refractive index for the blue was considerably less than for the green. In this last case the band was too ill-defined to admit of an accurate measurement of its position.

A preliminary examination of the light transmitted by a very thin film squeezed out between two plates of quartz, by means of a quartz spectrograph, showed that there was no return of transparency in the ultra-violet, at least up to wave-length  $\cdot 00028$  or thereabouts. To determine if possible the position of the centre of the band, which gives us  $\lambda_m$  in the dispersion formula, a series of photometric measurements

were made of the visible and ultra-violet light transmitted by a thin film deposited *in vacuo* by means of the cathode discharge. In the visible spectrum measurements were made by placing the glass plate, partly covered by the film, in contact with the double slit of a spectrometer, the line terminating the film being brought into coincidence with the junction of the slits. The thickness of the film was determined by means of fringe displacements, making use of the data obtained with the selenium prisms.

Owing to the difficulty of obtaining accurate data in the blue and violet by the visual method, and to enable us to carry on a study of the absorption in the ultra-violet, a photographic method was adopted, the details of which were worked out largely by Mr. Pfund.

The double slit was removed and a single slit put in its place, which was opened to a width of 0.5 mm. The ocular slit of the spectrophotometer was also opened to the same width. A short distance behind the ocular slit, the photographic plate was mounted with the selenium film covering the upper portion. A part of the plate was therefore exposed to light coming through clear glass, and part to light which had passed through the film of selenium. This method was found to give better results than a previous method which we tried, which consisted in substituting a photographic plate for the eyepiece of the instrument, and using the Vierordt slit as in the visual method. To determine the ratio of the intensities we made use of a photographic wedge, made by giving to a long narrow photographic plate an exposure decreasing uniformly in duration. To this strip a graduated scale was attached, and it was arranged to slide in a frame behind a narrow vertical aperture, against which the plate which had been exposed in the instrument, developed and dried, could be placed immediately below the wedge, which was then moved along until the spot of equal density was found. This spot could be determined to within 1 mm., the total length of the wedge being about 10 cms. In this way very good ideas of the relative intensities could be obtained, assuming Roscoe's rule governing the blackening of a plate to be true, as it probably is within the limits comprised in our experiments.

Below is given a table showing the values of  $\frac{I}{I'}$ , the ratio of the intensities, obtained by the two methods for a film the thickness of which was 0.0001 mm., and the calculated values of the extinction coefficient  $\kappa$ , defined by the equation

$$\frac{I}{I'} = e^{-\frac{4\pi\kappa d}{\lambda}},$$

where  $d$  is the thickness of the film and  $e$  the base of the natural logarithms.

	$\frac{I}{I'}$ (Visual).	$\frac{I}{I'}$ (Photographic).	$\kappa$ .
760	1.05	1.04	.0234
710	1.10	1.07	.0456
640	1.20	1.18	.0879
569	1.40	1.39	.155
550	1.80	1.80	.254
515	2.40	2.43	.358
490	3.40	3.44	.478
466	4.40	4.40	.571
442	6.20	6.15	.793
425	7.50	7.53	.877
415	9.50	9.46	.736
400	9.50	12.00	.785

The values of  $\kappa$  plotted as ordinates with wave-lengths as abscissæ give the extinction curve, which is reproduced on fig. 4 with the dispersion curve (p. 155).

To carry the work into the ultra-violet we abandoned the spectrophotometer with its glass prism and lenses, and made use of a short-focus concave grating with 14,000 lines to the inch. This grating was sent to me by Mr. Thorp of Manchester. It was made by mounting one of his celluloid replicas of a Rowland grating on a concave lens, the celluloid film being subsequently silvered. It was only intended as a device for illustrating the action of the concave grating\*,

\* I have mounted this grating on a light wooden frame designed according to the well-known Rowland device, which can be placed on the lecture-table and used for class illustration. The slit is illuminated with sun or arc light and the spectra received on a strip of ground glass. It is useful for showing how the spectra and the camera move relatively to each other.

but I found that if its aperture were reduced somewhat it gave surprisingly sharp lines.

A film of selenium was deposited on a thin plate of quartz, and mounted in front of the slit of the grating outfit, the lower half of the slit being covered with clear quartz, the upper half with quartz and selenium.

The slit was illuminated by a spark-discharge between zinc terminals, and the spectrum photographed. The absorbing action of the selenium manifested itself as a more or less complete obscuration of the upper half of the spectrum. By giving the selenium-covered portion of the slit a very long exposure, and the clear portion a short one, any given part of the spectrum could be balanced, the ratio of the times giving us an approximate value of  $\frac{I}{I'}$ .

We exposed a number of plates, and fully established the fact that the turning-point of the extinction curve, if it exists at all, lies beyond wave-length  $\cdot 00022$ . In the case of one plate the clear portion of the slit was exposed for 30 seconds, the selenium-covered portion for 62 minutes. The resulting photograph showed lines down to wave-length  $\cdot 00022$  for the clear part of the slit, while the selenium-covered part only recorded itself down to  $\cdot 00028$ , the lines being, however, very much fainter than the corresponding ones in the other half of the spectrum. The lines were of about the same intensity at wave-length  $\cdot 00033$ , for which we get, from the ratio of the times of exposure, the value  $1/124$  for  $I/I'$ . This gives us the value  $1\cdot 255$  for  $\kappa$ . The thickness of the film was the same as in the previous experiments. Still longer exposures would have to be given to balance the two halves of the spectrum for shorter waves than these, from which it is evident that the extinction curve is still rising rapidly at wave-length  $0\cdot 00022$ , where the coefficient has as high a value as in the case of the metals.

The extinction curve as figured is not to be regarded as very accurate, as no precautions were taken to eliminate the reduction in the intensity of the light due to the reflexion at the surface. In determining curves of absorption it is always better to use two films of different thickness. The errors in



the case of selenium may be considerable on account of the high refractive index, and I expect to redetermine the curve in the near future. In the present preliminary work the object was merely to determine whether there was a return to partial transparency in the ultra-violet region, which question appears to be answered in the negative, although a possible turning-point in the curve may be masked by the high reflexion coefficient. It appears to me to be extremely doubtful that there is but a single absorption-band in the present case, the more probable condition being a series of overlapping bands. We are in fact forced to this conclusion if we attempt to apply the dispersion formula to the results. Though we are unable to determine experimentally the value of  $\lambda_m$ , the wave-length corresponding to that at the centre of the absorption-band, we can calculate a value for it from three determinations of the refractive index in the region of comparative transparency. Writing the dispersion formula in the form\*

$$n^2 = m + \frac{m'\lambda^2}{\lambda^2 - \lambda_m^2}$$

we can calculate  $\lambda_m$  from

$$\lambda_m^2 = \frac{\lambda_3^2(\lambda_1^2 - \lambda_2^2) - \lambda_2^2(\lambda_1^2 - \lambda_3^2)C}{(\lambda_1^2 - \lambda_2^2) - (\lambda_1^2 - \lambda_3^2)C},$$

in which

$$C = \frac{n_3^2 - n_1^2}{n_2^2 - n_1^2},$$

where  $n_1$ ,  $n_2$ , and  $n_3$  are the values of the refractive index for wave-lengths  $\lambda_1$ ,  $\lambda_2$ , and  $\lambda_3$ . Applying this formula to the values determined by the prism method we find  $\lambda_m$  to be 0.00056, which we may assume to be not very far from the centre of the first band in the series. The true position of the centre of the first member of the series cannot be exactly determined, owing to the effects of the free periods of higher frequency, but the value given above can be considered a fair

\* "Dispersion of Ultra-Violet Rays," F. F. Martens, *Annalen der Physik*, No. 11, p. 612 (1901).

approximation. Ketteler has given a method for decomposing a complex absorption-band into its constituents; but as the process is very laborious and somewhat arbitrary, it has not seemed worth while to attempt to apply it until a more accurate curve has been determined.

If we take into account the first member of the series only, and apply the results obtained with the prisms to the formula

$$n^2 = b^2 + \frac{M_1}{\lambda^2 - \lambda_m^2},$$

from which the other formula may be derived by letting  $b^2 = m + m'$  and  $M_1 = m'\lambda_m^2$ , in which  $b^2$  is the dielectric constant, we find  $b^2$  to be very nearly 6.0. This latter form of the formula is the one generally used. If we use the original formula and determine  $m'$  and  $m$  from the expressions

$$m' = \frac{(n_s^2 - n_1^2)(\lambda_1^2 - \lambda_m^2)(\lambda_s^2 - \lambda_m^2)}{\lambda_m^2(\lambda_1^2 - \lambda_s^2)},$$

$$m = n_s^2 - \frac{m'\lambda_s^2}{\lambda_s^2 - \lambda_m^2},$$

we find

$$m = 5 \text{ and } m' = 1.02$$

or

$$b^2 = m + m' = 6.02.$$

If  $m$  in the original formula turns out to be greater than unity, it indicates that other absorption-bands must be taken into account. The dielectric constant of selenium has been measured by Romich and Nowack, the value found being 10.2.

The dielectric constant of a substance according to the electromagnetic dispersion theory is the dielectric constant of the æther, plus the dielectric constants of the various ions whose action on the æther waves gives rise to the phenomena of absorption and dispersion. Until the behaviour of selenium in the infra-red region has been investigated, it will be impossible to say whether the high value of the dielectric constant is due wholly, or only in part, to the ions whose free periods correspond in frequency to the green, blue, and ultra-violet rays. The infra-red work is already

under way, and until it is completed further discussion of the results given in the present paper is impossible\*.

The very high values of  $\kappa$  in the ultra-violet led me to look for traces of selective reflexion in this region. The light of an arc-lamp was reflected successively from six surfaces of selenium deposited on glass. The image of the crater after the sixth reflexion was very faint, but so far as the eye could judge without trace of colour. To determine whether or not ultra-violet light was present in excess, the light from the sixth surface was received upon a photographic plate one half of which was covered with a plate of glass which would absorb everything below wave-length 0.00034. The two halves of the plate were equally blackened, indicating that light of shorter wave-length than the above value was not present in any great excess.

Metals, however, have a much weaker reflecting power for ultra-violet radiations than for waves in the visible spectrum, and the failure to obtain traces of ultra-violet "Rest-strahlen" is doubtless due to related causes.

At the time when these experiments were tried the question of the possible detection of "Rest-strahlen" in the ultra-violet had never been discussed so far as I know. A paper has since appeared by Martens (*loc. cit.*) in which experiments are described which appear to prove that selective reflexion in the ultra-violet actually exists in certain circumstances.

We must be on our guard, however, against the error often made in assuming that the rays most strongly absorbed are identical with those most strongly reflected. This statement appears in so many of the text-books that it is well to call attention to the fallacy. Selective reflexion depends quite as much upon the refractive index of the medium as on the absorption. The index has a high value on the red side of the absorption-band, and a low value on the blue side; consequently the strongest reflexion will be for those rays on the red side of the centre of the absorption-band; that is to say

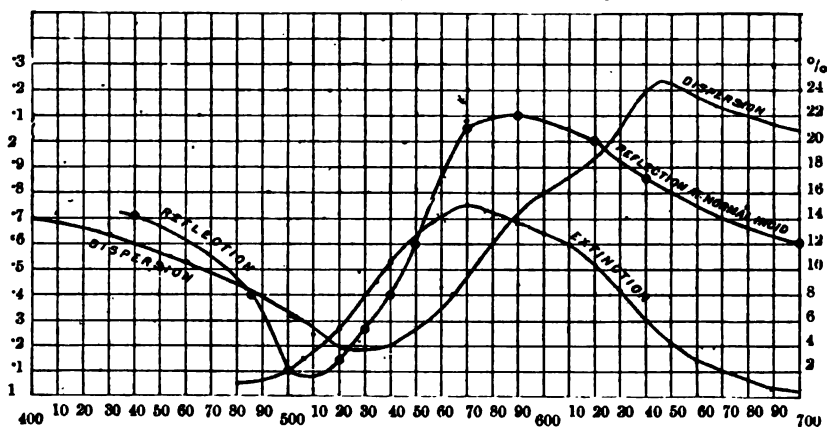
\* Since writing this paper, I have had the opportunity of examining the infra-red transmission up to wave-length  $23\mu$  with Prof. Mendenhall's very sensitive bolometer at the University of Wisconsin. No absorption-bands were found up to this point.

the maximum of the reflexion curve is shifted in the direction of the longer wave-lengths with respect to the absorption curve. The minimum of the reflexion curve lies on the blue side of the absorption-band, and in some cases may be equal to zero. The whole thing is of course contained in the formula for reflexion from absorbing media, which states that the percentage reflected,

$$R = \frac{n^2(1 + \kappa^2) + 1 - 2n}{n^2(1 + \kappa^2) + 1 + 2n}.$$

I have calculated from Pflüger's values of  $n$  and  $\kappa$  the reflexion curve which represents the surface colour of cyanine at normal incidence (fig. 5), which illustrates well the fact

Fig. 5.—Curve illustrating Surface-colour of Cyanine.



that the intensity of the reflected light in different parts of the spectrum is in no way a measure of the absorption. In point of fact, it is easily seen that the characteristic plum-colour of cyanine films is due rather to the almost complete *absence* of reflexion of the green rays than to strong metallic reflexion of any particular colour.

In the case of selenium, if we apply the reflexion formula to the data that have been obtained thus far, we obtain a curve which indicates that the reflexion increases rapidly with decreasing wave-length. As I have said before, multiple reflexions from selenium surfaces give no trace of colour,

which suggests that errors may exist in either the refraction or extinction curve. I have already pointed out where the source of trouble may lie in the case of the latter curve. In regard to the refraction-curve, it may be considered fairly accurate up to the point where the prism determinations stopped. In the case of films the thickness of which is less than the wave-length of light, I do not yet feel sure that the displacement of interference-fringes gives us a true measure of the refractive index. I hope some time to make a rigorous test of this point, for so far as I know it has never been settled.

The fact that the dispersion-curve of cyanine determined by the interferometer agreed so well with the curve obtained by means of a thin prism, does not prove conclusively that the method is not open to objection; for the same errors might occur in both cases: in other words, the deviation produced by a prism, the base of which was only a wave-length or two thick, might be affected by phase changes at the surfaces.

Selenium shows a strong surface-colour if the angle of incidence is in the neighbourhood of the polarizing angle, and the reflected light is examined through a nicol turned so as to extinguish as much as possible of the reflected light. The colour ranges from a greenish white through blue to deep violet as the angle of incidence increases.

The elliptical polarization of light reflected from selenium and the determination of the absorption and dispersion curves by the katoptric method is now in progress, as well as an investigation of the behaviour of the substance in the infra-red. It will be interesting to compare the results obtained in this way with the results obtained by the dioptric method.

The refraction and extinction curves for selenium, obtained by the katoptric method, are given in Ketteler's 'Theoretical Optics,' p. 552; but it is not stated whether the experiments were made with the glassy or metallic modification. The refraction curve in the red and orange region is obviously wrong, if it is intended to represent the dispersion of the glassy modification, as can be seen by comparing it with the curve obtained with the prisms.

## DISCUSSION.

Prof. S. P. THOMPSON exhibited some tellurium mirrors made in the same way as the selenium ones used by Prof. Wood.

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**XIII. *A suspected case of the Electrical Resonance of Minute Metal Particles for Light-waves. A New Type of Absorption. By R. W. WOOD, Professor of Experimental Physics in the Johns Hopkins University\*.***

CERTAIN experiments on which I have been engaged of late have led me to believe that I have found a new type of light absorption, which it may be possible to refer to the electrical resonance of small metallic particles for waves of light. The experiments of Garbasso and Aschkinass have shown that a plate of glass covered with uniformly arranged strips of tinfoil of equal size, which serve as resonators, shows the phenomenon of selective transmission and reflexion for electromagnetic waves of different wave-lengths. In other words, a plate of this description exhibits the electrical analogy of surface-colour. I have succeeded in producing metallic deposits on glass which the microscope shows to be made up of particles smaller than the wave-lengths of light, which by transmitted light exhibit colours quite as brilliant as those produced by aniline dyes. I have sought in every way to explain these colours, by all the well-known principles of interference and diffraction, and at the present am forced to accept the hypothesis suggested in the title of this paper, which I have chosen not without some misgivings.

In the present paper I shall content myself with giving a full account of the experimental data which I have thus far obtained, postponing for the present anything like a definite conclusion.

The metallic deposits are obtained by heating small fragments of the alkali metals in glass bulbs, thoroughly exhausted and hermetically sealed. Only the small portion of the bulb on which the metal particle lies is heated, leaving the

\* Read March 14, 1902.

remainder, where the condensation is to take place, quite cold. The metallic film which condenses on the wall, when viewed by transmitted light, shows colours of excessive brilliancy, as brilliant in fact as films strongly stained with aniline dyes. On first obtaining these films, I was of the opinion that these colours could be attributed in some way to interference, but more careful consideration showed that many difficulties were present. In the first place, the transmitted colours, in the case of thin plates, are never of any considerable intensity, being diluted with a large excess of white light. Moreover, the extraordinarily high absorption-coefficient of metallic sodium makes it impossible for us to apply the theory of the colours of thin plates, except on the assumption that the thickness of the film is exceedingly small in comparison with the wave-length, and that there is a relative change of phase at the two surfaces, which varies with the wave-length. This seemed on the whole not very probable, for, as far as experiments go, indications are that the phase-change in metallic reflexion is nearly independent of the wave-length. Moreover, metallic films obtained in other ways, as by chemical or cathodic deposition, do not show these colours. Thin films of metal show a more or less marked colour by transmitted light, but the colour is fixed for any definite metal, and, except in the case of gold and silver, not very pronounced. The sodium films, on the contrary, may be deep purple, blue, apple-green, or red according to conditions. I noticed at the outset that where the deposit was somewhat dense in the immediate vicinity of the sodium drop, the outside of the bulb, seen by reflected light, exhibited halo effects, similar to those shown by certain minerals. This pearly or silky lustre, which is difficult to describe, I at once recognized as a diffraction effect due to the scattering of light by small reflecting particles. Examination under the microscope showed this to be the case, the sodium having deposited on the glass in the form of small isolated drops. It at once occurred to me that the condition might be the same in the coloured films, the particles here being small enough to respond to the light-waves, in the same manner as the resonators of Garbasso and Aschkinass. I examined some of the more transparent of the coloured films, under a one-twelfth inch oil-immersion

objective, and found that my suspicions were verified, the films being made up of particles just barely visible as individual grains lying close together. I was unable to satisfy myself that the size varied with the colour of the film, and am of the opinion that if the resonance theory is the true one, the free period depends more on the proximity of the particles than on their actual size. The diameter of the particles, as measured with the micrometer, varies from about  $\cdot 0003$  to  $\cdot 0002$  mm. In other words, they are of about the size of the smallest micrococci described by the bacteriologists.

It occurred to me at first that the colours might be similar to those shown by mixed plates, which are explained in the same way as the coloured central images seen in certain transparent diffraction-gratings. This would, however, necessitate the presence of minute transparent particles of a thickness sufficient to give a retardation of  $\lambda/2$ . The formation of such particles could be conceived of as resulting from the oxidation of the sodium particles by a layer of absorbed air on the glass. It is therefore necessary to show at the outset that the cause of the colour is the presence of metallic sodium. That this is the case I feel sure, for if the slightest trace of air be allowed to enter the bulb, the colour, no matter how intense, instantly vanishes, the glass becoming as clear as before the formation of the film. The oxidation process could be made to take place slowly, by drawing out one end of the bulb into a long fine capillary, with a bore of about  $\cdot 01$  mm., and breaking off the end after the coloured film had been formed.

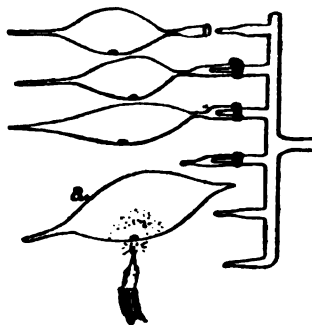
In certain cases it was observed that the colour changed before disappearing entirely. I also found that the colour of the film could be permanently changed by carefully heating the glass to a temperature just below that necessary to evaporate the film. Local heating to a slightly higher temperature drives off the film entirely, leaving the glass perfectly clear. By means of a small flame, it is possible to drive a patch of colour all over the inside of a bulb, and it is in this way that some of the best films are prepared. It was next found that cooling the films by the application of ice to the exterior of the bulb produced most extraordinary changes of colour. Pale green films, almost transparent, on being cooled ten or fifteen degrees, changed to a violet as deep as



that shown by dense cobalt-glass. Pink films were changed to deep blue-green, while films originally deep blue became transparent. These effects were most puzzling at first, but I finally succeeded in finding out the cause, as I shall show later on. At the beginning of the work it was almost impossible to predict what sort of a film would be obtained in any experiment. Sometimes, on first heating the sodium, a film of a deep claret colour would be obtained; once formed, it could be driven from one part of the bulb to another without any great change of colour. In another experiment, made under exactly the same conditions, so far as I could see, it was impossible to obtain anything but a deep blue. I prepared and experimented with fully fifty bulbs, without being able to arrive at any definite conclusion in regard to the conditions necessary for producing a definite result. It was finally found however, by blowing connected bulbs, that if the sodium was thoroughly boiled in one of them, and while still molten was shaken into an adjoining bulb, the surface of which was of course free from any deposit, on heating the globule in the fresh bulb, only blue films could be produced. This made it appear as if the claret-coloured film were produced by something volatile in the sodium which was driven off by the first heating. It was necessary, if possible, to find out what this was, for these red films were found to be more interesting than the blue, and it was desirable to be able to produce them at will. As a result of many experiments, I had formed a vague notion that bits of sodium cut from certain lumps in the bottle produced the red films on the first heating, while portions taken from other lumps did not. It seemed not unlikely that the sodium might contain potassium as an impurity, which might be the agent concerned. I accordingly prepared a set of bulbs containing potassium, and immediately found that magnificent reds and purples could be obtained at will; and I felt firmly convinced that the anomalies shown by sodium were due to potassium impurities. Similar coloured films could be obtained with lithium, though, owing to its higher boiling-point, bulbs of bohemian glass are required. Letting this serve as an introduction, it will be well to take up the experiments somewhat in detail.

As the optical behaviour of the films is extremely interesting, regardless of the ultimate cause of the colour, I shall describe in some detail the manner of preparing and filling the bulbs. It is in the first place a great economy of time if a number are exhausted at once. To accomplish this I have fitted the mercurial pump with a glass tube having half-a-dozen lateral branches drawn down as shown in fig. 1. The bulbs are

Fig. 1.



blown of the form shown in the same figure, and a piece of sodium or potassium is cut up under ligroin into blocks about 3 mm. on each edge. These are introduced into the bulbs as quickly as possible after wiping off the fluid, and the stems of the bulbs drawn down to a small bore for subsequent sealing.

They are quickly fastened to the branch tubes and exhausted. I find it a good plan to heat the metal until it fuses while the bulb is still on the pump; the whole bulb may be warmed by a Bunsen flame to drive off absorbed air. If the exhaustion is carried down to the point where the mercury begins to hammer, it is generally sufficient. The bulbs are now sealed off from the pump, and may be put away for future use, or experimented with at once. A burner should be made by drawing out a glass tube, which will give a pointed flame about half a centimetre high, and the tip of the flame allowed to play against the spot on the bulb where the metal lies (fig. 1, a). Sometimes the whole bulb will suddenly flash a deep violet or blue, and sometimes the film will develop more slowly. A chain of three or four bulbs may be made,

the sodium heated in one, and the clean molten metal shaken into the others, drops of various sizes sticking to the bulbs. Coloured films can then be formed by heating these clean drops in the bulbs. This shows that the oxide present in the first lump has nothing to do with the production of the colour.

I shall now take up in order and in some detail the appearances of the films by reflected and transmitted light, the spectral analysis of the light, the polarization effects, and the very remarkable temperature changes.

If the metal is heated at one end of a rather long tapering bulb, the colour is most intense near the metal and gradually fades away to nothing at the other end of the bulb. If the bulb is placed in strong sunlight with a black background, it is seen that in some places where the deposit is too slight to show much colour by transmission the light is scattered or diffused, and this diffused light is coloured. The claret-coloured or purple film, where the deposit is slight, scatters a green light, the surface appearing as if fluorescent. Now the spectrum of the transmitted light in these purple films has a heavy absorption-band in the yellow-green, consequently the scattered light is the complementary colour of the transmitted. If the film is greenish blue, the scattered light is reddish. The microscope shows that in these deposits, which have the power of scattering light, the individual particles are rather widely separated, that is, the distance between them is large in comparison to their diameters. I shall speak of this light as the "fluorescent" light, to distinguish it from the light scattered by the large particles, which is not coloured except by diffraction. This light, which gives the bulbs a slightly silky lustre where the particles are large, I shall call diffused light.

Returning now to the fluorescent light : in the case of the purple films, the appearance of a bulb in strong light is very much as if certain portions of its interior surface had been painted over with a solution of fluorescein. No trace of regular reflexion is shown by these films, except of course the reflexion due to the glass. The particles are so far apart that they apparently act as independent sources, the interference necessary for rectilinear propagation not being present. If the incident light is polarized, the fluorescent light is also

polarized, which is not the case for ordinary diffuse reflexion. On the resonance theory, we may regard this fluorescent light as the energy radiated from the resonators, as a result of their forced vibrations. Passing now to a part of the film where the colour of the transmitted light is deeper, we find that there is no longer any trace of this fluorescent light. The colour absent in the transmitted light is now regularly reflected, the particles being so close together that interference, as imagined by Huygens, takes place. In strong sunlight, this portion of the film shows neither the fluorescent nor the diffused (diffracted) light. Except at the spot where the regularly reflected image of the source of light appears, it is quite dark like the clear glass. Still farther down the bulb where the particles are very large, we get ordinary scattered light, and the film has the silky lustre to which I have alluded.

Summing up the results thus far, we find :—

Coarse particles diffract or scatter light, and give the bulb a silky lustre.

Minute particles very close together, regularly reflect those wave-lengths absent in the transmitted light, but give no scattered light.

Minute particles far apart, diffuse light of the same wave-lengths as those which are, to some extent, absent in transmitted light. This type of scattered light, which for convenience I have called fluorescent, is exhibited by deposits which are too scant to show any trace of colour when viewed by transmitted light.

### *Spectrum of the Transmitted Light.*

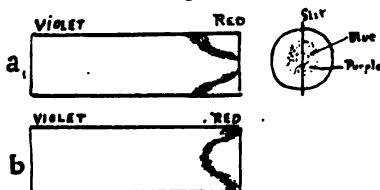
An examination of the transmitted light with a small direct-vision spectroscope showed that in some cases the films completely refused transmission of certain wave-lengths. The claret-coloured films had an absorption-band in the yellow, which was exceedingly black and quite narrow, its width rather less than one tenth of the easily visible spectrum. Any theory accounting for the colour of this film must explain the complete extinction of certain wave-lengths. In the case of the blue films, the absorption-band was in the red, but in this case it invariably appeared more diffused. The

green films apparently absorbed, more or less completely, the blue and red ends of the spectrum.

The changes of colour which accompany change of temperature are of two distinct types: a permanent change usually the result of local heating, and a temporary change, the result of cooling.

I was much puzzled by the fact that the change in colour was in the same direction in both cases; the region of absorption appearing to shift in the direction of greater wave-lengths. Purple-red films, with an absorption-band in the yellow, changed to blue, the change being due to the shifting of the band into the red. The effect can be best observed by touching the outside of the bulb with a hot glass rod. A transparent spot then appears where the metal has entirely evaporated, surrounded by a blue ring on a purple field. Placing the slit of the spectroscope along a diameter of the ring, the spectrum appears as in fig. 2, *a*. With potassium films, I have sometimes obtained permanent changes in the opposite direction; a violet-blue film becoming pink when heated, the spectrum appearing as in fig. 2, *b*. I do not feel sure that I have determined the exact cause of the permanent colour-changes, due to heating. It doubtless depends on the partial evaporation of the metallic particles, and we

Fig. 2.



must bear in mind that the period of vibration depends, not only on their size, but on the distance between them; both of which quantities will be affected by evaporation. The matter is probably further complicated by the fact that, in some cases, I have had films made up of particles of two different sizes. In this case it is not difficult to imagine that the smaller ones are completely vaporized, while the larger ones, which previously were of too great size to produce

colour, are brought down to dimensions small enough to enable them to resonate. This might explain the change from purple to blue. Experimental evidence is, however, rather against this hypothesis; and for the present I prefer to leave the cause of the permanent change in colour an open question.

The changes produced by cooling are much more startling, and of greater interest, for the cause has been discovered. We may summarize these effects something as follows:—Pink and purple films become blue when cooled, the original colour returning as soon as they are warmed up again. A pale green film becomes deep violet, while in some cases I have found that films, originally blue, become almost perfectly transparent when cooled, the blue colour returning subsequently. These effects are best shown by touching the outside of the bulb with a small piece of ice. At first sight, it seems as if the only possible effect of cooling would be a slight reduction of the size of the particles, and a contraction of the supporting wall. That this should be sufficient to affect the period of their vibration was almost unthinkable. If it were so, a further lowering of temperature should produce further changes, but I found that it was quite immaterial whether the bulb was touched with ice, or with a mixture of solid carbonic acid and ether; the resulting colour being the same in both cases. I have frequently obtained films so sensitive, that merely moistening the outside of the bulb and blowing upon it was sufficient to produce the change. On wiping it, or on stroking the bulb with the finger, the original colour would return. This was strongly suggestive of a molecular change, and for a while I was inclined to regard it as analogous to the well-known case of iodide of mercury. The final solution occurred to me in the following way. I had been for some time endeavouring to introduce into the bulb some fluid of high dielectric constant, to determine its effect on the colour. All fluids tried apparently contained sufficient oxygen to instantly bleach the films. The introduction of such a fluid should, it seemed to me, increase the capacity, slow down the period, and shift the absorption-band towards the red, or perhaps out of the visible spectrum entirely. Films had often been obtained which showed

absolutely no trace of colour-change on cooling, and it occurred to me that possibly traces of hydrocarbon vapour, from the ligroin in which the metal had been kept, might be condensed on the wall by the application of a cold body. I first prepared some films from sodium and potassium which had been heated for some time *in vacuo*, in order to remove all traces of the hydrocarbon. These films were invariably unresponsive, to either ice or solid carbonic acid. I next made a double bulb, and formed a film in the usual way in one of the bulbs. This film proved to be exceedingly sensitive to the application of ice, changing from apple-green to the colour of dense cobalt-glass. I now packed the other bulb in carbon dioxide and ether, in order to condense in it all of the suspected hydrocarbon vapour. It was then found that the film was no longer sensitive to the application of cold. To make absolutely sure that the true cause had been found, I cooled a small spot on a pink film to a low temperature by means of a small piece of carbon dioxide, which was left on the bulb for some time. The spot became almost colourless, the absorption having passed entirely out of the spectrum. On examining the spot quickly under the microscope, I had no trouble in seeing minute globules of a transparent liquid, sufficient quantity having condensed to form droplets. These grew rapidly smaller as the glass warmed, and the instant they disappeared, or perhaps a fraction of a second afterwards, the field of the instrument became first bluish, then pink, in consequence of the entrance of the absorption-band into the spectrum again.

There is a temperature effect of a different nature, which at first seems wholly inexplicable, but which I now think I understand. On one or two occasions I have had potassium films, originally deep violet, become almost transparent on the application of cold, and remain so *permanently*. What was still more remarkable, the appearance of the spot viewed in reflected light indicated clearly that the size of the particles had been increased, the spot showing the silky lustre to which I have already alluded, while the film surrounding it scattered no light at all. I had noticed that these films were apparently made up of two sets of particles—one set large enough to be seen under a low power, the other only coming into view under the highest power obtainable. After the temperature

change, the smaller ones seemed to have disappeared entirely; and I am now of the opinion that the condensation of the fluid film enabled them in some way to gather about and adhere to the larger particles, building up aggregates large enough to diffuse light.

*Changes produced by Oxidation.*

If the tip of one of the bulbs is cut off, the entrance of the air causes the coloured film to vanish like a flash. In some instances, I was of the impression that I detected a momentary change of colour before the film disappeared. To lengthen the process, I adopted the expedient of drawing the end of the bulb out into a long fine capillary, with a bore less than one one-hundredth of a millimetre. In this bulb a film of a deep pink colour was formed, and on cutting off the tip of the capillary the colour changed to blue, and the film vanished almost immediately. The small amount of air necessary to efface the films is indicated by the fact that at the end of an hour there was still a fairly good vacuum in the bulb, notwithstanding the fact that the end of the capillary had been open all the while. If the mouth of the capillary is fused immediately after the oxidation of the film, a new coloured film can be formed by heating the metal, the oxygen having been removed by the first film. This process can be repeated a number of times, showing that the presence of the oxide on the glass does not interfere with the deposition of the coloured film. If the process of oxidation be made very slow, by employing a very long capillary, and the process watched under the microscope, the black particles slowly become dim, and finally fade away. I am of the opinion that the microscope merely shows us the diffraction-disk due to the opaque particle. This would become dimmer as the size of the particle is reduced, without any apparent change of size. Examination with the spectroscope shows us that, during the process of oxidation, the absorption-band sometimes moves out of the spectrum through the red end, and sometimes merely fades away without any motion. I have tried filling the bulbs with carefully dried hydrogen gas, after the film had been formed, but the traces of oxygen present in the gas were sufficient to bleach the films. By employing two adjoining



bulbs, each lined with a coloured film, and cooling one of these in carbonic acid and ether, I was enabled to fill the bulbs with hydrogen at atmospheric pressure without destroying the coloured film in the cooled bulb. The low temperature prevented chemical action, and the oxygen was wholly removed by the film in the warmer bulb. On warming the bulb again, the colours persisted, showing that no change was produced by the presence of pure hydrogen.

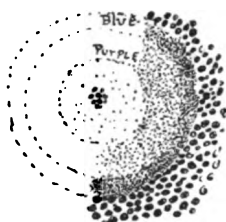
I find that it is even possible to fill a bulb with air at atmospheric pressure without destroying the colour, if the bulb is thoroughly cooled with the carbon dioxide and ether, the chemical action not taking place at this low temperature. These experiments were tried to test a certain theory of the cause of the colours which occurred to me one day, which it is not necessary to go into as it was found to be worthless. The extreme sensitiveness of these coloured films to minute traces of oxygen makes it seem probable that they will prove useful in the study of the flow of gases through small apertures and capillaries. I have noticed that if the capillary is exceedingly fine, the film, instead of disappearing all at once, gradually melts away, beginning at the end of the bulb near the capillary. Sometimes it is half-a-minute before the colour at the other end of the bulb bleaches out. It is as if a fluid were slowly rising in the bulb and dissolving the film. This seems rather surprising, in view of the ideas which we hold about the diffusion of gases in highly exhausted receivers.

*Relation between the Colour of the Film and the Size and  
Distribution of the Particles.*

One peculiarity of the coloured films is that the colour produced under a given condition seems to depend in some way on the condition of the glass surface on which the film is deposited. Circular pink spots are frequently found on a blue field, while sometimes circular spots quite devoid of colour are observed. The centre of the circle is usually occupied by a dark speck, which I believe to be a small particle of the metal thrown up when the globule is heated. This speck, strangely enough, seems to modify the nature of the surface of the glass over a circular area surrounding it, so that a film of a different colour forms on it, or in certain

cases no film at all forms. One of these spots which I studied under the microscope proved interesting. The black speck in the centre was found to be made up of a number of coarse particles of the metal lying close together. Surrounding this was a transparent ring, the particles here being very minute and very widely separated. Next came a ring of pinkish purple (absorption-band about at the D lines), while outside of this came a ring of deep blue (absorption-band in the red). The surrounding field was practically colourless, being made up of large particles similar to those at the centre of the ring (fig. 3). In the blue ring the particles were

Fig. 3.



distinctly closer together than in the pink one; a circumstance which I made sure of by having a number of other observers express an opinion on the matter. If now the particles are packed closer together in the blue film, we should expect the capacity to be increased, the same as by the introduction of the medium of high dielectric constant. The period would consequently become slower, and the absorption-band would lie further along towards the red, which is exactly what was observed. In some instances, I have been of the opinion that the particles in the blue films are larger than those in the pink ones, but of this I am not sure.

#### *Behaviour of the Films with Polarized Light.*

One of the first experiments which I tried with the deposits which were made up of particles large enough to scatter light, was their polarizing power. The angle of complete polarization in the case of non-metallic particles is  $90^\circ$ , as is well-known. J. J. Thomson (Recent Researches) has calculated the scattering effect of metallic spheres on light-waves, and has found that we should expect complete

polarization on a line making an angle of  $120^\circ$  with the direction of the incident light. I am not aware that any experiments have been made to test this calculation. The results which I obtained gave a value somewhat larger than this, the mean being about  $135^\circ$ . It is difficult, however, to get very accurate results with films deposited on spherical surfaces.

Very interesting results were obtained as soon as the coloured films were examined by polarized light. To enumerate all of the different effects which I have recorded in my note-book would require too much space, and I shall only mention two or three typical effects. The arrangement of the apparatus was as follows. The light of a Welsbach burner passed through a Nicol prism mounted in an opaque screen in such a way that it could be turned through a right angle, then through the coloured film at oblique incidence, and then into the direct-vision spectroscope. It was found in the case of one of the purple films, which had a strong absorption-band in the yellow-green, that this band was only present when the electric vector was parallel to the plane of incidence. When the electric vector was parallel to the surface the spectrum appeared continuous. In every case the colour was much more pronounced when the electric vector had a component normal to the surface. On turning the nicol from one position to the other, no motion of the absorption-band could be detected in this film, the change consisting in a gradual fading away. In other films, however, I have sometimes found that the absorption-band shifts its position when the nicol is turned. For example, in the case of a film which showed an absorption-band a little below the D lines with the electric vector perpendicular to the plane of incidence, on turning the nicol the band moved along into the red and became broader and fainter, the effect being similar to that produced by cooling the film.

When the films are viewed between two nicols more complicated effects are obtained, which I shall omit for the present as they have not yet been carefully studied.

Until someone has calculated the behaviour of a sheet of resonators at oblique incidence with reference to waves polarized in and at right angles to the plane of incidence,

it will be impossible to say whether the polarization experiments are in accordance with the resonance hypothesis or not. It seems to me, however, that the results obtained with polarized light will be the means of eventually determining the exact cause of the colours, or at least in deciding in favour of, or against, the theory of electrical resonance.

*Electrical Conductivity of the Films.*

The coloured films are apparently non-conducting. Inasmuch as it was difficult to make sure that the films were deposited up to and against the "sealed-in" electrodes, a bulb was fitted with a ground joint through which the wires passed as shown in fig. 4. After the film had been deposited the joint was turned, causing the tips of the wire to be drawn over the film. With a sensitive galvanometer in circuit with the bulb, 75 volts gave no deflexion when the wires were drawn over the film, though they scraped the glass clean of

Fig. 4.



the deposit. No change was produced in the appearance of the film between the wires with a potential-difference of 700 volts obtained from a storage-battery. With higher voltages a gas-discharge commenced, and the colour changed in the neighbourhood of the electrodes, owing to the heat. I have tried the effect of illuminating the films with the light of an arc brought close up to the bulb, but there is absolutely no trace of conductivity, even under these conditions. This is true even for deposits so dense, that under the microscope the particles appear to be in contact with, and even piled up on top of one another. A possible explanation of the absence of conductivity may be, that the granules consist of a metal core, surrounded by a non-conducting film of some sort, possibly oxide. I have noticed that bulbs, in which films have been repeatedly formed and driven off by the application of a flame, finally reach a state in which it is no longer possible to form coloured deposits, but I have not yet deter-

mined whether this is due to a modification of the surface of the glass, the removal of the oxygen, or some other cause. At the present time, I am studying the effects of the introduction of a small amount of liquid ligroin, which can be accomplished without impairing the vacuum, or destroying the coloured film, in the following way:—One end of the bulb is drawn out into a thin-walled tube with a bore of about 1 mm. After a satisfactory coloured film has been formed, a swinging motion of the arm drives the drop of molten metal down into the small tube, sealing it hermetically. The tip of the tube is then cut off under ligroin, which completely fills the tube, as far up as the plug. By means of a small flame, it is possible to close the mouth of the tube, the empty portion containing practically nothing but hydrocarbon vapour. On carefully warming the metal plug to the fusing-point, the hydrocarbon is discharged into the bulb, passing through the shell of liquid metal which adheres to the walls of the tube and removes from the fluid any impurities which are detrimental to the film. In this way, I have been able to introduce ligroin in quantities sufficient to thoroughly wet the inside of the bulb, and have obtained in this way colours of even greater brilliancy than before.

#### *Conclusion.*

At the present stage of the work, it seems to me that it is impossible to decide either in favour of, or against, the theory of resonance. Most of the changes produced by varying the conditions seem to be what we should expect. The idea of electrical resonance has, at all events, proved useful as a working hypothesis, for it led directly to the discovery of the cause of the changes produced by low temperatures. While I have obtained coloured films from sodium, potassium, and lithium, I have been unable to obtain them from thallium and cadmium, which give granular deposits very similar in other respects. I cannot help feeling that I shall eventually find some other explanation than the one ventured in the title of this paper, though I have been unable to conceive of any arrangement of media which will show colours of this nature by interference. At all events, it appears to me

that we have colour phenomena quite unlike any that are already known, and which are of some interest, regardless of the ultimate explanation which may be given them.

Baltimore, February 1, 1902.

#### DISCUSSION.

The Secretary read a letter from Prof. R. THRELFALL drawing the attention of the author to some experiments upon the same subject published by him in 1894. Particles of gold and platinum were deposited in a liquid, and good scattering of light obtained in all cases. The polarization-angle was exactly the same as with non-conducting particles. Prof. J. J. Thomson has shown that the peculiar scattering effect is only to be expected within very narrow limits as to size of particles. The colours observed by Prof. Wood should only be noticed when the particles have a very restricted size, and evidence in favour of or against the author's theory should be afforded by comparing the observed and calculated sizes of the particles. The value of the polarization-angle of the scattered light observed by Prof. Wood is evidence in favour of the theory suggested.

Mr. LUPTON pointed out that the experiments had probably been rendered difficult by the different colours in which the oxides of sodium and potassium can exist.

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#### XIV. *The Thermal Expansion of Porcelain.*

*By A. E. TUTTON, B.Sc., F.R.S.\**

THE thermal expansion of porcelain has formed the subject of several investigations during the last three years, and has become a subject of considerable importance in consequence of the employment of porcelain of the Bayeux and Berlin varieties for the reservoirs of air-thermometers.

The present investigation has been carried out with a specimen of Bayeux porcelain, which was kindly placed at the author's disposal by Prof. Callendar. It is of especial interest as being cut from the same tube which was employed (1 metre

\* Read March 14, 1902.

length of it) by Bedford in an investigation, by the method of Callendar, of the expansion of this variety of porcelain between  $0^{\circ}$  and  $830^{\circ}$  (Phil. Mag. vol. xlix. p. 90); and of which same tube also a piece was used by Chappuis in a series of determinations, by the Fizeau method, for the interval  $0^{\circ}$  to  $83^{\circ}$ . It was the fact of there being some discrepancy between the results of these observers that induced Prof. Callendar to suggest to the author the carrying out of an independent series of determinations, with the delicate interference-dilatometer described by the author to the Royal Society in the year 1898 (Phil. Trans. A. vol. cxc. p. 313, and vol. cxcii. p. 455).

The interference-dilatometer in question possesses all the advantages over the original Fizeau apparatus of the Bureau International des Poids et Mesures, Sèvres, of that devised by Abbe and elaborated by Pulfrich (*Zeitschr. für Instrumentenkunde*, 1893, p. 365); together with further improvements on the Abbe form. Two of these improvements are of considerable importance, namely, the separation of the observing part of the apparatus from the expansion-chamber, and its removal to an adequate distance from the heated atmosphere above the bath in which the latter is heated; and the measurement of the temperature of the interference tripod, and the substance under investigation which it carries, by means of a thermometer bent just above the cylindrical bulb and so arranged that the latter lies on the platinum-iridium tripod table, in tied contact with one of the screws supporting the glass cover-disk, and only a millimetre distant from the substance itself. For the author has proved by direct experiment that a thermometer merely hung alongside in the bath does not register the temperature of the tripod, which at the higher limit of  $120^{\circ}$  may be as much as  $3^{\circ}$  lower. The chief advantages over the Fizeau apparatus are briefly: (1) The employment of a micrometric method of measuring the position and width of the interference-bands; (2) the use of autocollimation; (3) the employment of C hydrogen light instead of sodium light, as being more truly monochromatic and not subject to secondary interference; and (4) an arrangement of the thermal chamber which readily permits an extension of the range to an upper limit of  $120^{\circ}$ .

The author's method also renders the observer independent of the nature of the surface of the substance investigated, as to whether it is polishable or not. This is attained by the use of the aluminium compensator, a relatively thick disk of aluminium laid on the top of the substance. It is thus the upper surface of this disk, and not that of the substance, which, together with the under surface of the glass cover-disk, reflects the interfering red hydrogen light. As aluminium expands about 2.6 times as much as platinum-iridium, it is easy to choose a disk, out of a series prepared for the purpose, which will roughly compensate for the expansion of the lengths of the platinum-iridium screws, which project above the table of the same alloy on which the substance rests. By so doing, approximately the whole expansion of the substance is recorded by the movement of the interference-bands, affording at once an idea of its relative expansibility, or in the case of contraction indicating the fact. The author's value (quoted later) for the expansion of aluminium agrees fairly well with that given by Fizeau, and it has been proved that any error introduced by the use of this third substance cannot exceed  $\pm 0.02$  of an interference-band, an amount far less than the differences observed between the numbers of bands afforded by successive determinations under identical conditions. The aluminium compensator is simply invaluable when substances incapable of good polish are being investigated, and "biscuit" porcelain is eminently such a case; and there is the further advantage in the case of a piece of tube, of which the section is only an annulus, that there is a large field of bands afforded instead of a mere ring showing parts of bands. The polish taken by aluminium is pre-eminently suitable, as the intensity of the reflected light is about the same as that from the cover-glass. The compensators keep unimpaired if stored in a desiccator. As some misapprehension has arisen as to the use of the compensator, the author wishes to emphasize the fact that no accession of accuracy is claimed for the method, and, as has just been shown, it may introduce  $\pm 0.02$  of error; but as this latter is absolutely negligible, the other advantages referred to are such as to make its use in the specified cases most convenient and valuable. Given, however, a substance capable of taking



a good polish, and whose thermal deformation is approximately known, the compensator is both unnecessary and inadvisable. The reflecting surface of the aluminium disk used in these determinations was minutely concave, affording bands slightly curved. This is an advantage, as it enables the observer to know at once whether expansion or contraction is occurring, according as the bands move from or to their centre of curvature.

The specimen of Bedford's tube used by Chappuis was 15 mm. long, and was furnished at its two ends with plane surfaces. The one placed uppermost was polished as far as possible, and the fringes of sodium light obtained with this annulus were used for his determinations.

The author had an ample amount of Bedford's tube to furnish three specimens for investigation. They were cut in lengths somewhat over 12 mm. and ground with truly plane ends by Messrs. Troughton and Simms, the makers of the dilatometer. It was not found possible to get a satisfactory polish; and this has been shown to be unnecessary. Portions of the two ends were then ground out somewhat, at three places in each case, leaving three equidistant small patches of the original truly plane end, so that the specimens might stand with three-point contact on the truly plane polished surface of the platinum-iridium table (that side of the table being employed which was not furnished with projecting points). Likewise the aluminium disk lay, when put into position, with three-point contact on the upper porcelain blunt points. The diameter of the pieces of porcelain was about 17 mm., and the walls were about 3 mm. thick and fairly uniform, the hole being as nearly as possible central.

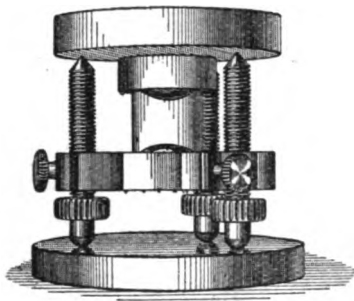
The arrangement of the tripod and its contents will be clear from the accompanying illustration (fig. 1, p. 186).

Three independent determinations were carried out with each piece of porcelain, each occupying seven to eight hours. The method followed was precisely that described in the memoir on the "Thermal Deformation of the Crystallized Sulphates of Potassium, Rubidium, and Cæsium" (Phil. Trans. 1899, A. vol. xcii. p. 467).

Only the very slightest signs of inequality of expansion were observed, as indicated by a just perceptible amount of

rotation of the bands, nothing like so much as is described by Chappuis for the fringes of the annular rim, and usually it was only temporary, the original position being regained

Fig. 1.



before the close of each half of the determination, after constancy at the two higher limiting temperatures in the neighbourhood of  $60^{\circ}$  and  $120^{\circ}$  was attained.

The results of the determinations, together with the necessary data, are set forth in the tables on pp. 188, 189.

$L_t$  represents the length of the specimen of porcelain, as measured at the ordinary temperature by the author's thickness-measurer (Phil. Trans. A, vol. cxc. p. 337, 1898). It is the length at the central axis, immediately under the minute silvered ring on the under side of the glass cover-disk, the centre of which is the point of reference for the micrometric measurement of the initial and final positions of the bands for each interval of temperature.

$l_a$  is the thickness of the aluminium disk at the centre of reference.

$l$  represents the mean length of the three platinum-iridium screws, or vertical distance between silver ring and surface of platinum-iridium table.

$d$  is the thickness of the air-layer at the centre of reference.

$t_1$  is the initial temperature; in every case it was the temperature of the room (as determined by the thermometer in contact with the tripod) at the moment of commencing the determination, about 6.30 A.M. in mid-winter, after the apparatus had been left 16-17 hours since completing on the previous day either adjustment or a determination. It was

considered more satisfactory to start with a lower limit of this constant character, than to attempt to approach nearer zero by artificial cooling, as is the method at the Bureau International.  $t_2$  is the limiting temperature of the first interval, and  $t_3$  that of the second interval.  $t_2 - t_1$  is considered the first interval,  $t_3 - t_1$  the second.

$b_1$ ,  $b_2$ , and  $b_3$  are the corresponding barometric pressures, required for computing the correction to the observed number of bands.

$f_1$  is the observed number of bands for the first interval, and  $f_2$  for the second.

The small correction which follows is that which has to be applied for the alteration of the refractive index of air due to change of temperature and pressure. It is fully discussed on p. 349 of the memoir (*loc. cit.*) on the dilatometer. The formula is

$$f' = f + d(t_2 - t_1) \cdot \frac{b_1}{760} \cdot \frac{1}{1 + \alpha t_1} \cdot \frac{1}{1 + \alpha t_2} \cdot 2 \frac{(n-1)\alpha}{\lambda} \\ - d(b_2 - b_1) \cdot \frac{1}{1 + \alpha t_2} \cdot 2 \frac{n-1}{760\lambda};$$

where  $f$  represents the observed and  $f'$  the corrected number of bands,  $\alpha$  the coefficient of expansion of air, and  $n$  the refractive index of air for the wave-length  $\lambda$  of the light employed.  $f'_1$  and  $f'_2$  are consequently the corrected numbers of bands for the two intervals.

Then follows the actual amount of diminution of thickness of the air-layer, as given by the product  $f'\lambda/2$ , where  $\lambda/2$  is 0.0003281 mm.

The expansion of the platinum-iridium screws and of the aluminium compensator are next given, calculated from the formulæ (*vide* Phil. Trans. A, vol. cxc. pp. 353 & 356, for determinations of these coefficients):—

$$\text{For the screws, } l \left[ 10^{-9} \left( 8600 + 4.56 \frac{t_1 + t_2}{2} \right) \right] (t_2 - t_1),$$

$$,, \quad \text{aluminium, } l_a \left[ 10^{-8} \left( 2204 + 2.12 \frac{t_1 + t_2}{2} \right) \right] (t_2 - t_1),$$

for the first interval, and substituting  $t_3$  for  $t_2$  for the second interval.

*Expansion of Bayeux Porcelain.—Specimen 1.*

$L_t=12.259$ mm. $l_a=8.187$ mm. $l=20.907$ mm. $d=0.461$ mm.			
	Determination 1.	Determination 2.	Determination 3.
Temperatures ...	$\begin{cases} t_1 & \dots\dots 60.8 \\ t_2 & \dots\dots 63.4 \\ t_3 & \dots\dots 120.8 \end{cases}$	$\begin{cases} 10.0 \\ 64.7 \\ 122.2 \end{cases}$	$\begin{cases} 11.9 \\ 64.6 \\ 120.9 \end{cases}$
Bar. pressures ...	$\begin{cases} b_1 & \dots\dots 761.2 \text{ mm.} \\ b_2 & \dots\dots 760.9 \\ b_3 & \dots\dots 760.6 \end{cases}$	$\begin{cases} 753.7 \text{ mm.} \\ 753.1 \\ 752.5 \end{cases}$	$\begin{cases} 755.2 \text{ mm.} \\ 756.1 \\ 757.0 \end{cases}$
No. of bands ...	$\begin{cases} f_2 & \dots\dots 7.38 \\ \text{Corrn.} & \dots\dots -0.08 \\ f_2' & \dots\dots 7.30 \\ f_3 & \dots\dots 17.42 \\ \text{Corrn.} & \dots\dots -0.14 \\ f_3' & \dots\dots 17.28 \end{cases}$	$\begin{cases} 6.97 \\ -0.08 \\ 6.89 \\ 17.14 \\ -0.14 \\ 17.00 \end{cases}$	$\begin{cases} 6.83 \\ -0.07 \\ 6.76 \\ 16.72 \\ -0.13 \\ 16.59 \end{cases}$
Dim. of thickness of air-layer ...	$\begin{cases} f_2 \lambda/2 & \dots\dots 0.0023951 \text{ mm.} \\ f_3 \lambda/2 & \dots\dots 0.0056696 \end{cases}$	$\begin{cases} 0.0022606 \text{ mm.} \\ 0.0055778 \end{cases}$	$\begin{cases} 0.0022180 \text{ mm.} \\ 0.0054433 \end{cases}$
Exp. of Pt.-Ir. ...	$\begin{cases} \text{1st int.} & \dots\dots 0.0103662 \\ \text{2nd int.} & \dots\dots 0.0211900 \end{cases}$	$\begin{cases} 0.0100297 \\ 0.0203805 \end{cases}$	$\begin{cases} 0.0096676 \\ 0.0202885 \end{cases}$
Exp. of Al. ...	$\begin{cases} \text{1st int.} & \dots\dots 0.0105577 \\ \text{2nd int.} & \dots\dots 0.0218323 \end{cases}$	$\begin{cases} 0.0102247 \\ 0.0215323 \end{cases}$	$\begin{cases} 0.0098592 \\ 0.0209247 \end{cases}$
Excess exp. Al. ...	$\begin{cases} \text{1st int.} & \dots\dots -0.0001915 \\ \text{2nd int.} & \dots\dots -0.0006428 \end{cases}$	$\begin{cases} -0.0001950 \\ -0.0006518 \end{cases}$	$\begin{cases} -0.0001916 \\ -0.0006362 \end{cases}$
Expansion of Porcelain. ...	$\begin{cases} L_t - L_t & \dots\dots 0.0022036 \\ L_t - L_t & \dots\dots 0.0050268 \end{cases}$	$\begin{cases} 0.0020656 \\ 0.0049260 \end{cases}$	$\begin{cases} 0.0020264 \\ 0.0048071 \end{cases}$
	$\begin{cases} \theta & \dots\dots 0.000\ 032\ 618 \\ \phi & \dots\dots 0.000\ 000\ 089\ 94 \\ L_0 & \dots\dots 12.2588 \text{ mm.} \end{cases}$	$\begin{cases} 0.000\ 029\ 784 \\ 0.000\ 000\ 106\ 81 \\ 12.2587 \text{ mm.} \end{cases}$	$\begin{cases} 0.000\ 030\ 777 \\ 0.000\ 000\ 100\ 34 \\ 12.2586 \text{ mm.} \end{cases}$
	$\begin{cases} a & \dots\dots 0.000\ 002\ 661 \\ b & \dots\dots 0.000\ 000\ 007\ 34 \end{cases}$	$\begin{cases} 0.000\ 002\ 430 \\ 0.000\ 000\ 008\ 71 \end{cases}$	$\begin{cases} 0.000\ 002\ 511 \\ 0.000\ 000\ 008\ 19 \end{cases}$
Mean values .....	$a=0.000\ 002\ 534.$ $b=0.000\ 000\ 008\ 08.$		

*Expansion of Bayeux Porcelain.—Specimen 2.*

$L_t=12.334$ mm. $l_a=8.187$ mm. $l=20.645$ mm. $d=0.124$ mm.			
	Determination 1.	Determination 2.	Determination 3.
Temperatures ...	$\begin{cases} t_1 & \dots\dots 5.5 \\ t_2 & \dots\dots 61.4 \\ t_3 & \dots\dots 120.7 \end{cases}$	$\begin{cases} 7.2 \\ 62.2 \\ 121.7 \end{cases}$	$\begin{cases} 5.7 \\ 63.1 \\ 123.2 \end{cases}$
Bar. pressures ...	$\begin{cases} b_1 & \dots\dots 771.1 \text{ mm.} \\ b_2 & \dots\dots 770.8 \\ b_3 & \dots\dots 770.5 \end{cases}$	$\begin{cases} 768.5 \text{ mm.} \\ 768.5 \\ 768.5 \end{cases}$	$\begin{cases} 769.3 \text{ mm.} \\ 769.2 \\ 769.2 \end{cases}$
No. of bands ...	$\begin{cases} f_2 & \dots\dots 7.34 \\ \text{Corrn.} & \dots\dots -0.02 \\ f_2' & \dots\dots 7.32 \\ f_3 & \dots\dots 17.52 \\ \text{Corrn.} & \dots\dots -0.04 \\ f_3' & \dots\dots 17.48 \end{cases}$	$\begin{cases} 7.30 \\ -0.02 \\ 7.28 \\ 17.81 \\ -0.04 \\ 17.77 \end{cases}$	$\begin{cases} 7.38 \\ -0.02 \\ 7.36 \\ 17.97 \\ -0.04 \\ 17.93 \end{cases}$

Specimen 2 (*continued*).

	Determination 1.	Determination 2.	Determination 3.
Dim. of thickness $\left\{ \begin{array}{l} f_2 \lambda/2... \\ \text{of air-layer} \dots \left\{ \begin{array}{l} f_2 \lambda/2... \end{array} \right. \end{array} \right.$	0-0024017 mm. 0-0057352	0-0023886 mm. 0-0058304	0-0024148 mm. 0-0058829
Exp. of Pt.-Ir. $\left\{ \begin{array}{l} \text{1st int.} \dots \\ \text{2nd int.} \dots \end{array} \right.$	0-0101925 0-0211373	0-0099444 0-0210237	0-0103770 0-0215744
Exp. of Al. $\dots \left\{ \begin{array}{l} \text{1st int.} \dots \\ \text{2nd int.} \dots \end{array} \right.$	0-0105065 0-0220486	0-0102556 0-0219412	0-0106997 0-0225159
Excess exp. Al. $\left\{ \begin{array}{l} \text{1st int.} \dots \\ \text{2nd int.} \dots \end{array} \right.$	-0-0003140 -0-0009113	-0-0003112 -0-0009175	-0-0003227 -0-0009415
Expansion of Porcelain $\dots \left\{ \begin{array}{l} L_2-L_1... \\ L_2-L_1... \end{array} \right.$	0-0020877 0-0043239	0-0020774 0-0049129	0-0020921 0-0049414
$\theta \dots$	0-000 031 447	0-000 031 780	0-000 030 029
$\phi \dots$	0-000 000 082 63	0-000 000 086 32	0-000 000 093 29
$L_0 \dots$	12-3338 mm.	12-3338 mm.	12-3338 mm.
$a \dots$	0-000 002 550	0-000 002 577	0-000 002 435
$b \dots$	0-000 000 008 70	0-000 000 007 00	0-000 000 007 56
Mean values .....	$a=0-000 002 521.$	$b=0-000 000 007 09.$	

*Expansion of Bayeux Porcelain.—Specimen 3.*

$L_1=12-208$  mm.  $l_0=8-187$  mm.  $l=20-549$  mm.  $d=0-154$  mm.

	Determination 1.	Determination 2.	Determination 3.
Temperatures $\dots \left\{ \begin{array}{l} t_1 \dots \\ t_2 \dots \\ t_3 \dots \end{array} \right.$	$8^{\circ} \cdot 4$ $62^{\circ} \cdot 2$ $122^{\circ} \cdot 8$	$10^{\circ} \cdot 4$ $63^{\circ} \cdot 8$ $125^{\circ} \cdot 5$	$7^{\circ} \cdot 5$ $61^{\circ} \cdot 7$ $123^{\circ} \cdot 0$
Bar. pressures $\dots \left\{ \begin{array}{l} b_1 \dots \\ b_2 \dots \\ b_3 \dots \end{array} \right.$	764-9 mm. 764-7 764-5	764-2 mm. 764-3 764-5	762-9 mm. 762-8 762-7
No. of bands $\dots \left\{ \begin{array}{l} f_2 \dots \\ \text{Corrn.} \dots \\ f_1' \dots \\ f_2' \dots \\ \text{Corrn.} \dots \\ f_3' \dots \end{array} \right.$	7-20 -0-03 7-17 17-90 -0-05 17-85	7-03 -0-03 7-00 17-96 -0-05 17-91	7-22 -0-03 7-19 18-12 -0-05 18-07
Dim. of thickness $\left\{ \begin{array}{l} f_2 \lambda/2... \\ \text{of air-layer} \dots \left\{ \begin{array}{l} f_2 \lambda/2... \end{array} \right. \end{array} \right.$	0-0023525 mm. 0-0058587	0-0022967 mm. 0-0058764	0-0023501 mm. 0-0059288
Exp. of Pt.-Ir. $\left\{ \begin{array}{l} \text{1st int.} \dots \\ \text{2nd int.} \dots \end{array} \right.$	0-0096855 0-0209204	0-0096225 0-0210737	0-0097542 0-0211174
Exp. of Al. $\dots \left\{ \begin{array}{l} \text{1st int.} \dots \\ \text{2nd int.} \dots \end{array} \right.$	0-0100371 0-0219452	0-0099795 0-0221269	0-0101056 0-0221483
Excess exp. Al. $\left\{ \begin{array}{l} \text{1st int.} \dots \\ \text{2nd int.} \dots \end{array} \right.$	-0-0003516 -0-0010248	-0-0003570 -0-0010532	-0-0003514 -0-0010309
Expansion of Porcelain $\dots \left\{ \begin{array}{l} L_2-L_1... \\ L_2-L_1... \end{array} \right.$	0-0020009 0-0048319	0-0019397 0-0048232	0-0020077 0-0048979
$\theta \dots$	0-000 031 315	0-000 029 613	0-000 030 987
$\phi \dots$	0-000 000 083 25	0-000 000 090 45	0-000 000 087 50
$L_0 \dots$	12-2077 mm.	12-2077 mm.	12-2078 mm.
$a \dots$	0-000 002 565	0-000 002 426	0-000 002 538
$b \dots$	0-000 000 008 82	0-000 000 007 41	0-000 000 007 17
Mean values.....	$a=0-000 002 510.$	$b=0-000 000 007 13.$	

The slight excess of expansion on the part of the aluminium over that of the screws, acts like the expanding porcelain in diminishing the thickness of the air-layer, and has therefore to be deducted from the total observed diminution; the resulting differences represent the amounts of expansion of the porcelain for the two intervals. Then follow the calculations of the two constants  $a$  and  $b$  of the coefficient of expansion of porcelain. For the discussion of the formulæ employed, and the mode of deriving them, the memoir on the dilatometer should be consulted (*loc. cit.* p. 352). It will be sufficient here merely to state the formulæ, which are as follows:—

$$\theta = \frac{(t_1 + t_2)(L_{t_2} - L_{t_1})}{(t_2 - t_1)(t_3 - t_2)} - \frac{(t_1 + t_2)(L_{t_3} - L_{t_1})}{(t_3 - t_1)(t_3 - t_2)},$$

$$\phi = \frac{L_{t_2} - L_{t_1}}{(t_2 - t_1)(t_3 - t_2)} - \frac{L_{t_3} - L_{t_1}}{(t_3 - t_1)(t_3 - t_2)},$$

$$L_0 = L_{t_1} - \theta t_1 - \phi t_1^2,$$

$$a = \frac{\theta}{L_0}, \quad b = \frac{\phi}{L_0}.$$

The results for the three pieces of porcelain tube are compared in the following table, and the final mean result for the linear expansion of Bayeux porcelain is given at the foot.

	<i>a.</i>	<i>b.</i>
Specimen 1. ....	0·000 002 534	0·000 000 008 08
„ 2. ....	2 521	7 09
„ 3. ....	2 510	7 13

Final mean values:  $a = 0·000 002 522$ ,  $b = 0·000 000 007 43$ .

This investigation, therefore, affords as the mean coefficient of linear expansion,  $a + bt$ , of Bayeux porcelain, between  $0^\circ$  and  $t^\circ$ , within the limits of  $0^\circ$  and  $120^\circ$ , the value

$$10^{-9}(2522 + 7·43t).$$

That is,

$$L_t = L_0[1 + 10^{-9}(2522t + 7·43t^2)].$$

The true coefficient,  $\alpha$ , of linear expansion at  $t^\circ$ , or the mean coefficient between any two temperatures (within the limits

of  $0^\circ$  and  $120^\circ$ ) whose mean is  $t$ , is as follows :—

$$\alpha = a + 2bt = 0.000\,002\,522 + 0.000\,000\,014\,86t;$$

or  $10^{-9}(2522 + 14.86t).$

The mean coefficient of the cubical expansion between  $0^\circ$  and  $t^\circ$ , for the same limits of  $0^\circ$  and  $120^\circ$ , derived from this investigation, is :

$$\alpha + bt = 0.000\,007\,566 + 0.000\,000\,022\,29t;$$

or  $10^{-9}(7566 + 22.29t).$

That is

$$V_t = V_0[1 + 10^{-9}(7566t + 22.29t^2)].$$

The actual coefficient of cubical expansion,  $\alpha$ , at any temperature  $t$ , within the limits  $0^\circ$  to  $120^\circ$ , and also the mean coefficient of cubical expansion between any two temperatures (within the same specified limits) whose mean is  $t$ , is expressed by

$$\alpha = a + 2bt = 10^{-9}(7566 + 44.58t).$$

The value obtained by Bedford for the linear expansion for the interval  $0^\circ$  to  $600^\circ$  was as follows :—

$$L_t = L_0[1 + (3425t + 1.07t^2)10^{-9}],$$

and  $\alpha = a + 2bt = (3425 + 2.14t)10^{-9}.$

Beyond  $600^\circ$  the formula does not accurately reproduce the observations, which were carried out as far as  $830^\circ$ .

For the cubical expansion Bedford gives :

$$V_t = V_0[1 + (10275t + 3.24t^2)10^{-9}],$$

and  $\alpha = a + 2bt = (10275 + 6.48t)10^{-9}.$

The result obtained by Chappuis for the linear expansion between  $0^\circ$  and  $83^\circ$  was the following :—

$$L_t = L_0[1 + (2824.1t + 6.17t^2)10^{-9}],$$

$$\alpha = a + 2bt = (2824.1 + 12.34t)10^{-9}.$$

And for the cubical expansion :

$$V_t = V_0[1 + (8472.4t + 18.53t^2)10^{-9}],$$

$$\alpha = a + 2bt = (8472.4 + 37.06t)10^{-9}.$$

The considerable difference thus presented between the results of Bedford and Chappuis is most striking with regard

to the increment of the coefficient, the constant  $b$  in the linear expansion being six times greater according to Chappuis than according to Bedford. The constant  $a$  is at the same time reduced.

The results now presented by the author agree tolerably well with those of Chappuis, but emphasize this difference, the constant  $b$  being seven times larger than according to Bedford, and the constant  $a$  slightly smaller than according to Chappuis.

In the following table are set forth the actual coefficients of linear expansion at particular temperatures, for every  $10^\circ$  up to the limit of the determinations, deduced from the observations of the author and of Chappuis respectively. The actual lengths when  $L_0=1$  are also graphically expressed by the two curves in fig. 2 (the dotted one representing the results of Chappuis), for which degrees of temperature are taken as abscissæ and the lengths as ordinates.

Table showing Values of  $\alpha = a + 2bt$  for various Temperatures.

Temperature.	Tutton.	Chappuis.
0	0·000 002 522	0·000 002 824
10	2 671	2 947
20	2 819	3 071
30	2 967	3 194
40	3 116	3 317
50	3 265	3 441
60	3 414	3 564
70	3 562	3 688
80	3 711	3 811
90	3 859	
100	4 008	
110	4 157	
120	4 305	

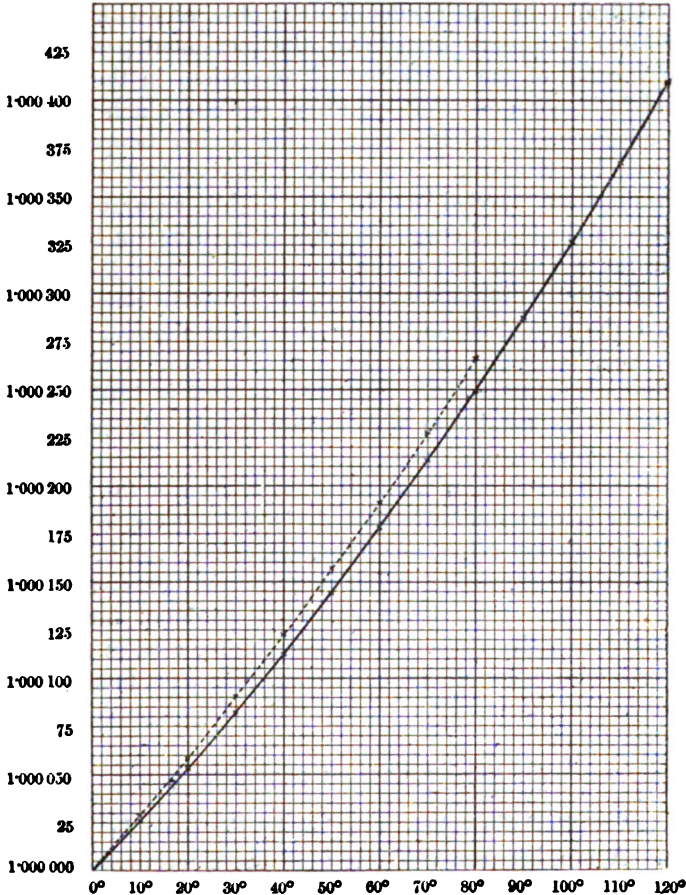
The value for  $120^\circ$ , calculated from the formula of Chappuis, is 0·000 004 305, exactly the same as the author's value.

Chappuis offered, towards an explanation of the difference between Bedford's results and his own, the observation that some rotation of the fringes occurred, indicating inequality of expansion and curving of the tube; and further, that the hole through the tube was considerably eccentric, so that opposite parts of the wall presented variations in thickness, and the effect of a glaze differing in expansibility from the



"biscuit" might be to slightly deform the tube on heating. In the author's opinion this is not the cause of the discrepancy, for in the author's experiments the amount of rotation of the interference-bands was negligible, and the hole was central.

Fig. 2.—Lengths at  $t^{\circ}$  when  $L_0=1$ .



The results now presented indicate rather that the discrepancy is due to a fundamental real difference, dependent on the interval of temperature for which the determinations were made. They indicate clearly, in the author's opinion, that the character of the expansion between 0° and 100° is substantially that exhibited by the results of Chappuis for the

interval of  $0^{\circ}$  to  $83^{\circ}$ , those results, however, not going quite far enough in their difference from those of Bedford; also, that the considerable difference from the latter observer's values is owing to the large interval included by Bedford's,  $0^{\circ}$  to  $830^{\circ}$ . In other words, presuming the accuracy of Bedford's results (and there is every reason to do so, as they are confirmed by the results of other observers with Berlin porcelain), it appears proved that the increment per degree ( $\Delta\alpha/\Delta t = 2b$ ), of the coefficient of expansion, in the case of porcelain is not a constant quantity, but one which is much larger between  $0^{\circ}$  and  $100^{\circ}$  than at the higher temperatures explored by Bedford. Two entirely independent series of determinations, carried out by the highly accurate interference method, and employing the quite different forms of apparatus of Fizeau and the author, involving also the use of light of entirely different wave-lengths, have now conclusively settled the rate of expansion for the short interval of  $0^{\circ}$  to  $100^{\circ}$ , and, indeed, if the author's higher limit is included, for the interval  $0^{\circ}$  to  $120^{\circ}$ . The temperature of  $120^{\circ}$  herein attained, is the maximum which can with safety be employed in an interference-dilatometer.

The conclusion now arrived at with respect to Bayeux porcelain is very similar to that derived from a research by Holborn and Day (*Ann. der Phys. und Chem.* vol. ii. p. 505, 1900), on the expansion of Berlin porcelain between  $0^{\circ}$  and  $1000^{\circ}$ . A rod of unglazed porcelain 483 mm. long was employed, and the method of the comparator used in making the determinations of its expansion. It was found that between  $250^{\circ}$  and  $625^{\circ}$  the results are fairly reproduced by the expression

$$l_t = l_0 [1 + (2954t + 1.125t^2)10^{-9}].$$

But below  $250^{\circ}$  the values afforded by the formula are too high. Again, between  $700^{\circ}$  and  $900^{\circ}$  the determinations are not accurately reproduced by the formula; but agreement becomes better again at  $1000^{\circ}$ .

Prof. Callendar, in discussing the relative results of Chappuis and Bedford (Proceedings of the Physical Society, Nov. 22nd, 1901), stated that "Bedford's results agreed very fairly, allowing for difference of material, with Holborn and Day's from  $200^{\circ}$  to  $600^{\circ}$ , and that both differed from those of

Chappuis between  $0^{\circ}$  and  $80^{\circ}$  when extrapolated in a precisely similar manner. It was quite possible, as he (Prof. Callendar) had previously suggested, that the expansion of porcelain between  $0^{\circ}$  and  $100^{\circ}$  was anomalous. It appeared certain that some anomaly in the expansion at  $800^{\circ}$  was indicated in the experiments of Bedford, and also in those of Holborn and Day."

The supposition of Prof. Callendar, as to an anomalous expansion between  $0^{\circ}$  and  $100^{\circ}$  in the case of porcelain, appears to be well founded, the anomaly consisting in a very much larger increment for this interval than for the higher interval  $200^{\circ}$  to  $600^{\circ}$ . The author fully agrees with Dr. Chappuis that the thermal expansion of the porcelain employed for air-thermometers, whether of the Bayeux or Berlin varieties, cannot be represented by a two-term function throughout an interval of temperature exceeding a very few hundred degrees. On no account can such an expression be safely employed outside the interval for which it was actually determined, extrapolation leading to grave errors in the case of porcelain.

#### DISCUSSION.

The Secretary read a letter from Dr. P. E. SHAW stating that the accuracy of the micrometer readings seemed to depend more on the distinctness of the rings than on anything else. He asked if the author considered mercury or hydrogen light better than sodium light, and if the error in the present research was less than  $\frac{\lambda}{25}$ , which is supposed to represent the accuracy of the Abbe-Fizeau method.

Dr. CHREE expressed his interest in the paper because of its bearing on the measurement of temperature by the gas-thermometer, in which case it is essential to know the coefficient of expansion of the porcelain bulb. He did not consider the behaviour of porcelain anomalous because an irregular expansion might be expected. In the case of Jena glasses used in thermometry, the value of  $a$  and  $b$  determined between  $0^{\circ}$  and  $100^{\circ}$  are different to those obtained when the range is extended to  $200^{\circ}$  C. He was surprised at the differences between Bedford and Chappuis and Tutton, and said that the evidence was in favour of the instruments used by the latter observers. It would be interesting if the author could

obtain Chappuis' specimen of porcelain and repeat his experiments between  $0^{\circ}$  and  $80^{\circ}$ .

Mr. TUTTON, in reply to Dr. Shaw, said that the bands were perfectly distinct when using red hydrogen light. He did not use mercury light because of the necessity of constantly heating the tube.

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XV. *On the Temperature Variation of the Electrical Resistances of Pure Metals, and Allied Matters.* By W. WILLIAMS, B.Sc., Municipal Technical College, Swansea\*.

MANY of the physical properties of metals are periodic functions of their atomic weights. This is especially true of the valency and atomic volume. In a lesser degree it is also true of the melting-point and electric resistance. Now, the periodic variations of these four quantities for most of the metals can be very simply related to one another. For if  $\sigma$  is the specific resistance, at  $0^{\circ}$  C.,  $m$  the maximum chemical valency,  $V$  the atomic volume, and  $T$  the absolute melting-point, to a first approximation  $\sigma = \frac{KmV}{T}$ , where  $K$  is a quantity which appears to have different values for different groups of metals. Dr. Fleming has already pointed out that the metals of large specific resistance are those having large atomic volumes and large valencies. For silver, copper, magnesium, zinc, cadmium, thallium, lead, mercury (in the solid state), and probably calcium,  $K = 1.72 \times 10^8$  if  $\sigma$  is measured in microhms for a centimetre cube, and  $V$  is the quotient of the atomic weight by the density. For gold, indium, tin, and aluminium, however,  $K$  has only half this value. For sodium and potassium also its value appears to be half that given above; while for arsenic, antimony, and bismuth it is about double.

In the table that follows,  $\sigma$  is the value calculated for the specific resistance at  $0^{\circ}$  C. from  $\frac{KmV}{T}$ , while  $\sigma'$  is the value obtained by observation. The maximum chemical valency is as given by the Periodic Law, except in the case of gold and copper, where the values 3 and 2 are taken as being

\* Read March 14, 1902.

more consistent with the chemical characteristics of the metals.

	m.	V.	T.*	$\sigma$ .	$\sigma'$ .	Diff.
Silver.....	1	10.2	1173	1.5	1.5	0 p. cent.
Copper .....	2	7.1	1333	1.82	1.7	7 "
Magnesium .....	2	13.9	1023	4.6	4.1	12 "
Zinc .....	2	9.1	676	4.65	5.8	20 "
Cadmium .....	2	12.9	503	7.5	7.5	0 "
Thallium .....	3	17.2	561	15.9	17.6	9.6 "
Lead .....	4	18.1	605	20.6	20.0	3 "

\* The melting-points are as given in Nernst's '*Chemistry*.'

The resistance of a metal is approximately proportional to the absolute temperature. Hence  $\sigma = \frac{K}{273} \cdot \frac{mV\theta}{T}$ , where  $\theta$  is the absolute temperature, so that the specific resistance in the solid state at the temperature of fusion is  $\frac{KmV}{273}$ . Now, the resistance of pure mercury in the solid state has been very carefully investigated by Dr. Fleming (Proc. Royal Society, vol. lx. No. 359, p. 79). According to his results, the process of fusion appears to set in at  $-50^{\circ}\text{C}$ ., and is not properly completed until  $-36^{\circ}\text{C}$ . is reached, the value of  $\sigma'$  at  $-50^{\circ}\text{C}$ . just before fusion begins being 21. By calculation, taking  $m$  to be 2, and  $V=14.1$ , we get 17.8. Again, at  $-95^{\circ}\text{C}$ . ( $-100^{\circ}\text{C}$ . on the *pt* scale), the calculated value is 14.4, Dr. Fleming's value being 15.5.

The melting-point of calcium is not definitely given. The metal, however, is said to melt at "red heat," and will therefore have a melting-point between  $500^{\circ}\text{C}$ . and  $600^{\circ}\text{C}$ ., so that  $T$  is about 853. Hence,  $m$  being 2 and  $V$  25.4,  $\sigma=10.6$ , Matthiessen's value being 7.5 †.

Taken as a whole, the accordance between  $\sigma$  and  $\sigma'$  is not unsatisfactory, being about the same as the accordance observed in the case of the law of Dulong and Petit as to atomic heat. Thus, taking 6.3 for the constant of that law, the value is 15 per cent. above it in the case of calcium, and 20 per cent. below it in the case of sulphur. Also, considering the wide variations that occur in the values of  $m$ ,  $V$ ,  $T$ , and  $\sigma$ , the accordance cannot be regarded as a matter of

† The melting-point of calcium is probably underestimated,  $800^{\circ}\text{C}$ ., or 1073 absolute being perhaps more nearly correct.

accident, but must be taken as an indication of a definite physical law.

Certain metals, however, fail to conform with the relation for  $\sigma$  although they are closely related, both physically and chemically, to those that do. Thus gold, indium, tin, and aluminium fail, although the first is allied to copper and silver, the second to thallium, and the third to lead. Thus:—

	<i>m.</i>	V.	T.	$\sigma$ .	$\sigma'$ .
Gold .....	3	10.1	1310	3.99	2.0
Indium .....	3	15.3	449	17.64	8.4
Tin.....	4	16.3	503	22.05	10.5
Aluminium .....	3	10.6	923	5.94	2.9

The metals of the alkali and arsenic groups also fail. Thus:—

	<i>m.</i>	V.	T.	$\sigma$ .	$\sigma'$ .
Potassium .....	1	45.4	335	23.4	8.4
Sodium .....	1	23.7	369	11.1	5.1
Arsenic .....	5	13.2	773	14.8	35.1
Antimony .....	5	17.9	710	21.7	43.1*
Bismuth .....	5	21.1	538	33.9	108.0

According to Pictet, if  $\alpha$  is the coefficient of thermal expansibility,  $V\frac{1}{2}\alpha T$  is a constant for metals. Calling this constant  $c$ , we get the following for its values in the case of the metals discussed above:—

	V.	$\alpha$ .	T.	$c$ .
Silver.....	10.2	.0000194	1173	.0486
Copper .....	7.1	.0000170	1333	.0436
Gold .....	10.1	.0000147	1310	.0417
Magnesium .....	13.9	.0000270	1023	.0684
Zinc .....	9.1	.0000208	676	.0421
Cadmium .....	12.9	.0000316	593	.0440
Tin.....	16.3	.0000230	503	.0293
Thallium .....	17.2	.0000302	561	.0437
Aluminium .....	10.6	.0000222	923	.0450
Indium .....	15.3	.0000417	449	.0465
Lead .....	18.1	.0000290	605	.0461

\* For antimony,  $\sigma' = 45.8$  according to Lorenz, and 40.3 according to Berget.

Excluding magnesium and tin, the probable value of the constant is  $\cdot 045$ .

The alkali metals appear to constitute a separate group having a different value for  $c$ , thus,

	V.	$\alpha$ .	T.	$c$ .
Sodium .....	23.7	$\cdot 000072$	369	$\cdot 0763$
Potassium.....	45.4	$\cdot 000083$	335	$\cdot 0992$

The mean value for  $c$  being  $\cdot 088$ , or about double its value for copper, &c. The arsenic metals, or at least bismuth and antimony, also appear to constitute a separate group, having  $c = \cdot 021$  or half its value for copper, &c. Thus,

	V.	$\alpha$ .	T.	$c$ .
Antimony .....	17.9	$\cdot 0000116$	710	$\cdot 0215$
Bismuth .....	21.1	$\cdot 0000137$	538	$\cdot 0204$

On account of the irregularities of the metal, the result in the case of arsenic cannot be taken as definite \*.

Now, the groups that are thus characterized by different values for  $c$  are also characterized by corresponding values for  $K$ . Thus, where  $c = \cdot 045$ ,  $K$  is  $1.72 \times 10^2$ . Where  $c$  is approximately ( $\frac{1}{2} \times \cdot 045$ ),  $K$  is approximately  $2 \times 1.72 \times 10^2$ , and where  $c$  is approximately ( $2 \times \cdot 045$ ),  $K$  is approximately ( $\frac{1}{2} \times 1.72 \times 10^2$ ). This suggests that the relation for  $\sigma$  can be rendered more comprehensive if written

$\sigma = \frac{A}{273} \cdot \frac{mV\theta}{cT}$ , where  $A$  is a constant. Thus modified, the relation gives the following values for  $\sigma$ :—

	Observed.	Calculated.
Silver.....	1.5	1.5
Copper .....	1.7	2.0
Magnesium .....	4.1	3.4
Sodium .....	5.1	7.1
Zinc .....	5.8	5.36
Cadmium .....	7.5	7.95
Potassium .....	8.4	11.5
Thallium .....	17.6	17.7
Lead .....	20.0	21.7
Arsenic .....	35.1	34.3
Antimony .....	43.1	50.2
Bismuth.....	108.0	80.1

\* The metal sublimes when heated and has a definite melting-point only under pressure.

Except in the case of sodium, the order in which the metals stand is the same as regards the observed and calculated values of  $\sigma$ ; and although the differences are great in the case of some of the metals, the values are throughout of the proper order of magnitude. The modified relation fails to hold, however, for gold, indium, tin, and aluminium, so that these metals, as before, are exceptional. Whether it holds for calcium and mercury cannot be ascertained until the value of  $c$  can be obtained for those metals. If they follow Pictet's law, so that  $c$  lies between  $\cdot 04$  and  $\cdot 05$ , they will conform with the relation in its modified form to the same degree of approximation as they do in the case of the original one.

If  $m$ , in the relation for  $\sigma$ , is to be the maximum valency according to the Periodic Law, the relation will approximately hold for platinum and palladium. Thus :

	V.	$m$ .	T.	$c$ .	$\sigma$ .	$\sigma'$ .	Diff.
Palladium.....	9.2	8	1775	.0411	8.44	10.2	17 p. cent.
Platinum .....	9.1	8	2050	.0379	7.82	9.0	13 "

The metals of the platinum and palladium groups have a valency of 4 in their sesqui- and tetra-chlorides. Ruthenium and osmium, however, form potassium compounds analogous to chromates, manganates, and ferrates, in which the valency must be 6. In addition, they form tetroxides  $\text{RuO}_4$  and  $\text{OsO}_4$ , indicating a valency of 8 in accordance with the Periodic Law, a valency that also accords with the potassium compounds  $\text{K}_2\text{PtCl}_6$ , and  $\text{K}_2\text{PdCl}_6$ . It therefore appears that a maximum valency of 8 is not incompatible with the chemical characteristics of the metals.

The metals of the Iron Group do not conform with the relation for  $\sigma$ , a matter to be fully dealt with on a future occasion.

According to the law of Dulong and Petit,  $s$  is approximately  $\frac{6.3}{w}$ , where  $s$  is the specific heat and  $w$  the atomic weight. Also,  $V = \frac{w}{d}$ , where  $d$  is the density. Hence  $V = \frac{6.3}{sd}$ . Again, if  $\alpha$  is the coefficient of thermal expansibility, supposed to be constant, and if  $\lambda = V^{\frac{1}{2}}\alpha\theta$  and  $c = V^{\frac{1}{2}}\alpha T$ ,



we get

$$\sigma = \frac{A}{273} \cdot \frac{nV\theta}{cT} = \frac{Bm\lambda}{c^2sd} = \frac{Bm\lambda}{c^2n\rho} = \frac{Bm\lambda\theta}{c^2nh}.$$

where  $B$  is a constant,  $n$  the average number of atoms per unit volume,  $\rho$  the atomic specific heat, and  $h$  or  $(\rho\theta)$  the average thermal energy of an atom at temperature  $\theta$ . Now,  $V$  is proportional to the average space assigned to an atom at the absolute zero. Hence  $\lambda$  or  $V^{\frac{1}{3}}\alpha\theta$  will be proportional to the average relative displacement of the centres of two neighbouring atoms between absolute zero and the temperature  $\theta$ , which we may call the average atomic displacement at temperature  $\theta$ .

If  $\alpha$  is constant, so that  $\lambda$  for any metal is proportional to  $\theta$ , and if  $\rho$  is also constant,  $\sigma$  must be proportional to  $\theta$ , so that  $\frac{\sigma}{\sigma_0} = \frac{\theta}{273} = 1 + \epsilon$ , where  $\sigma$  and  $\sigma_0$  are the values at  $t^\circ$  C. and  $0^\circ$  C. respectively, and  $\epsilon = .003665$ . According to this, the temperature resistance-coefficients of all pure metals must be the same, namely  $\frac{1}{273}$ , and the resistance must vanish at the absolute zero. The investigations of Fleming and Dewar, however, have shown that while the resistance tends to vanish at the absolute zero, the temperature-coefficient is usually higher than  $\frac{1}{273}$ , its average value being about .004. Now we know that  $\alpha$  and  $\rho$  are not constant, but slowly increase with rise of temperature. Hence the view suggests itself that the deviation of the temperature-coefficients from the simple value  $\frac{1}{273}$  may be due to the temperature-variations of  $\alpha$  and  $\rho$ .

Since the relation  $\sigma = \sigma_0(1 + \epsilon t)$  is true to a first approximation for all pure metals, we can put

$$\frac{\sigma}{\sigma_0} = \frac{\theta}{273} \phi(\theta) = (1 + \epsilon t)(1 + \gamma t + \eta t^2 + \dots),$$

which suggests that temperature enters into the relation for  $\sigma$  in two ways essentially different, namely:

(1) Directly, as an essential factor, and represented above by  $\frac{\theta}{273}$ ; and

(2) Indirectly, and represented above by  $\phi(\theta)$ , as the temperature-variation of one or more of the other essential factors.

We have then to inquire whether these essential factors can be  $\alpha$  and  $\rho$ , and whether  $\phi(\theta)$  can be built up from their temperature-variations.

According to Prof. J. J. Thomson ('Nature,' May 10th, 1900), the specific resistance of a metal on the electronic theory is given by

$$\sigma = \frac{2\mu n^2}{qe^2l^3},$$

where  $q$  is the average number of electrons dissociated in unit volume per unit time,  $\mu$  is the mass of an electron,  $e$  its electrical charge,  $u$  its average velocity of translation, and  $l$  the length of its mean free path. Hence, since  $\mu$ ,  $e$ , and  $l$  are constant as regards temperature, the temperature-variation of  $\sigma$  must depend upon the temperature-variations of  $u$  and  $q$ . On this matter, Prof. J. J. Thomson makes the following observation:—"If we suppose that  $u$ , the mean velocity of translation of the corpuscles, varies with the temperature in the same way as the velocity of translation of the molecules of a gas,  $\mu u^2$  would be proportional to the absolute temperature, and the specific resistance would, considered as a function of the absolute temperature  $\theta$ , vary as  $\frac{\theta}{q}$ ; if  $q$ , the amount of ionization, increases as the temperature increases, the resistance will vary more slowly than the absolute temperature; if  $q$  diminishes as the temperature increases, the resistance will vary more rapidly than the temperature." Hence, according to Prof. J. J. Thomson, in the temperature relation  $\frac{\sigma}{\sigma_0} = \frac{\theta}{273} \phi(\theta)$ , the factor  $\frac{\theta}{273}$  enters in the determination of the average velocity of translation of the moving electrons, while  $\phi(\theta)$  enters as the temperature-variation of the electronization-coefficient  $q$ .

But  $\sigma \propto \frac{m\lambda\theta}{c^2nh}$ . Hence  $\frac{\sigma}{\sigma_0} = \frac{\theta}{273} \cdot \frac{\lambda\lambda_0}{\lambda_0h}$ , so that  $\phi(\theta) = \frac{\lambda\lambda_0}{\lambda_0h}$ , and therefore, since according to Prof. J. J. Thomson  $\phi(\theta) = \frac{q_0}{q}$ , we must have  $q \propto \frac{h}{\lambda}$ . This result, taken in conjunction with  $\sigma \propto \frac{m\lambda\theta}{c^2nh}$ , suggests that  $q \propto \frac{nh}{m\lambda}$ . That is, that for the metals that conform with the relation for  $\sigma$ , the electronization per unit volume increases with the average thermal energy of the

atom and the number of atoms per unit volume, and decreases with the average relative displacements of the atoms and their maximum chemical valency.

The investigations of Fleming and Dewar have shown that  $\phi(\theta)$  is not a linear function of  $\theta$ . If, however, we confine ourselves to a limited range, say from  $0^\circ$  C. to  $100^\circ$  C., we may consider it to be approximately linear, and so considerably simplify the matter. In that case we get  $\sigma = \sigma_0(1 + \epsilon t)(1 + \gamma t) = \sigma_0(1 + at + bt^2)$ , where  $a = (\epsilon + \gamma)$ , and  $b = \epsilon\gamma$ . As might be expected, this temperature-factor fails to hold both at very high and at very low temperatures, but may be taken to hold with a considerable degree of accuracy between  $0^\circ$  and  $100^\circ$ , the only range within which the temperature-variations of  $\alpha$  and  $\rho$  can be said to be fairly accurately known.

Let  $\alpha$  and  $s$  be linear functions of the temperature, which is sufficiently accurate for our present purpose, and let  $\alpha = \alpha_0(1 + \beta t)$  and  $s = s_0(1 + \delta t)$ , where  $\alpha$  and  $s$  are the values at  $t^\circ$  C.,  $\alpha_0$  and  $s_0$  at  $0^\circ$  C., and  $\beta$  and  $\delta$  the temperature-variations. Then

$$\lambda = V^{\frac{1}{2}} \alpha_0 \left[ \left( 1 - \frac{273\beta}{2} \right) + \frac{1}{2}\beta t \right] (273 + t),$$

$$h = \rho_0 \left[ \left( 1 - \frac{273\delta}{2} \right) + \frac{1}{2}\delta t \right] (273 + t);$$

and therefore,

$$\begin{aligned} \phi(\theta) &= \frac{h_0 \lambda}{h \lambda_0} = \frac{1 + \frac{1}{2}\beta' t}{1 + \frac{1}{2}\delta' t} \\ &= 1 + \frac{1}{2}(\beta' - \delta')t - \frac{1}{8}\delta'(\beta' - \delta')t^2 + \&c., \end{aligned}$$

where  $\beta' = \frac{\beta}{1 - \frac{273\beta}{2}}$ , and  $\delta' = \frac{\delta}{1 - \frac{273\delta}{2}}$ .

Thus  $\gamma = \frac{1}{2}(\beta' - \delta')$ ,  $\eta = -\frac{1}{8}\delta'(\beta' - \delta')$ , &c., and in the approximate temperature-factor  $\frac{\sigma}{\sigma_0} = 1 + at + bt^2$ , which holds between  $0^\circ$  and  $100^\circ$ ,  $a = \epsilon + \frac{1}{2}(\beta' - \delta')$  and  $b = \frac{1}{2}\epsilon(\beta' - \delta')$ .

This result, however, cannot at present be subjected to any reliable and decisive test. For the accurate investigation of the temperature-variation of  $\alpha$  over wide ranges of temperature has not been made for pure metals, while, though various observers have investigated the temperature-variations of  $s$ , there is a considerable want of accordance between the

results obtained. The accurate determination of both thermal expansibility and specific heat are matters of very great difficulty, trifling differences in the values of either quantity producing very serious differences in the values of the temperature-variations deduced from them. Thus, according to Naccari, the specific heat of copper at  $100^{\circ}$  C. is  $\cdot 09422$ , and  $\cdot 09634$  at  $200^{\circ}$  C. Assuming the latter value to be only  $\frac{1}{2}$  per cent. too high, the value at  $200^{\circ}$  C. would be  $\cdot 09586$ . In the former case the temperature-variation is  $\cdot 0000212$ , in the latter  $\cdot 000016$ ; so that a difference of only  $\frac{1}{2}$  per cent. per  $100^{\circ}$  in the value of  $s$  produces a difference of 30 per cent. in the value of the temperature-variation. Now, apart altogether from experimental difficulties, which are certainly very considerable, differences greater than this can arise in the values of  $s$  at the same temperature of different specimens of the same metal from differences in mechanical qualities alone. Unless, therefore, the value of  $\sigma$ ,  $\alpha$ , and  $s$  are accurately determined *for the same specimen and over a considerable range of temperature*, we cannot expect a close and definite relation to exist between their temperature-variations. Hence, as the experimental information has to be collected from different observers for different specimens, probably in different mechanical conditions, we must be satisfied if the relation  $\gamma = \frac{1}{2}(\beta' - \delta')$  yields values of the proper order of magnitude, differing from those obtained experimentally by no more than those values for the same metals according to different observers differ from one another.

In spite, however, of the imperfections of the experimental data available to test the matter, enough appears to be known to show that  $\phi(\theta)$ , for many of the metals, is *mainly* determined by  $\beta$  and  $\delta$ , that the probable form of the function is  $\frac{1 + \frac{1}{2}\beta t}{1 + \frac{1}{2}\delta t}$ , and that  $\gamma = \frac{1}{2}(\beta' - \delta')$ , as the following results will show.

In selecting experimental data respecting  $\beta$  and  $\delta$ , the results of Fizeau by the interferometer method have been taken for  $\alpha$  between  $0^{\circ}$  and  $100^{\circ}$ ; these being taken because they depend upon measurements susceptible of more accurate determination than those of other methods.

As regards specific heats, the results of Naccari (1888) have principally been followed.

Naccari's values for  $s$  are as follows—the values at  $0^\circ$  C. being calculated from the values given at  $100^\circ$  C.,  $200^\circ$  C., and  $300^\circ$  C. :—

	$0^\circ$ .	$100^\circ$ .	$200^\circ$ .	$300^\circ$ .	$\delta$ .
Copper .....	·0921	·09422	·09634	·09846	·0002302
Silver.....	·05449	·05663	·05877	·06091	·0003927
Cadmium .....	·0548	·0570	·0594	·0617	·0004385
Lead .....	·02972	·03103	·03244	·03380	·0004575
Zinc .....	·0906	·0951	·0996	·1040	·0004967
Aluminium .....	·2116	·2211	·2306	·2400	·0004489

Naccari's results for copper are not in accord with those of Bedè and Trowbridge. Thus, according to Bedè, the mean value of  $s$  between  $15^\circ$  and  $100^\circ$  is ·09331 ; ·09483 between  $16^\circ$  and  $172^\circ$  ; and ·09680 between  $17^\circ$  and  $247^\circ$ . Hence, the average value of  $\delta$  is ·000516. Again, according to Trowbridge ('Science Abstracts,' Dec. 1898), the mean value of  $s$  between  $-181^\circ$  and  $13^\circ$  is ·0868, and ·094 between  $23^\circ$  and  $100^\circ$ . Hence the average value of  $\delta$  is ·000546.

Naccari gives no results in the case of tin. Lorenz gives the following :  $s$  at  $0^\circ$  = ·05368 ; at  $50^\circ$  = ·05534 ; at  $75^\circ$  = ·05643. Hence the average value of  $\delta$  is ·00064.

Naccari's results for aluminium are confirmed by those of Richards. Thus, according to Richards, the mean value of  $s$  between  $0^\circ$  and  $100^\circ$  is ·2270 ; ·2370 between  $0^\circ$  and  $300^\circ$  ; and ·2520 between  $0^\circ$  and  $600^\circ$ . Hence the average value of  $\delta$  is ·000463.

Fizeau's values for  $\alpha$  are as follows— $\alpha_{40}$  denoting the value at  $40^\circ$  C., and  $\alpha_{50}$  that at  $50^\circ$  C. :—

	$\alpha_{40}$ .	$\alpha_{50}$ .	$\beta$ .
	·0000	·0000	
Copper .....	1678	1698	·001251
Silver.....	1921	1936	·000806
Cadmium .....	2069	3102	·001124
Lead .....	2924	2948	·000848
Zinc .....	2918	2915	
Aluminium .....	2313	2336	·001086
Tin.....	2234	2269	·001671

According to Fizeau, zinc behaves in an anomalous manner as regards its thermal expansibility, the value of  $\alpha$  being

greater at  $40^\circ$  than at  $50^\circ$  C. This, however, is not in accord with the observations of Matthiessen, according to whose results for zinc,  $l = l_0[1 + \cdot 00002741t + \cdot 0000000234t^2]$ , where  $l$  and  $l_0$  are the lengths of the same bar at  $t^\circ$  and  $0^\circ$  respectively. Hence  $\beta = \cdot 00172$ . For most of the metals, however, for which both Matthiessen and Fizeau give values, Fizeau's values for  $\beta$  are about half those deduced from Matthiessen's observations. Thus :

	Matthiessen.	Fizeau.	Ratio.
Copper .....	$\cdot 0025$	$\cdot 00125$	2.0
Silver.....	$\cdot 00149$	$\cdot 000806$	1.85
Cadmium .....	$\cdot 00354$	$\cdot 001124$	3.15
Tin.....	$\cdot 00259$	$\cdot 001671$	1.55
Lead .....	$\cdot 00543$	$\cdot 000848$	$\cdot 64$
Palladium .....	$\cdot 00184$	$\cdot 00088$	2.09
Gold .....	$\cdot 00165$	$\cdot 000567$	2.91
Platinum .....	$\cdot 000823$	$\cdot 000923$	$\cdot 89$

Mean = 1.89

Fizeau's values for copper and aluminium are confirmed by those of Dulong and Petit, and Mr. Tutton. Thus, according to Dulong and Petit, the mean value of  $\alpha$  for copper between  $0^\circ$  and  $100^\circ$  C. is  $\cdot 00001718$ , and  $\cdot 00001883$  between  $0^\circ$  and  $300^\circ$ . Hence  $\beta = \cdot 00101$ . Again, according to Mr. Tutton (Proc. Royal Society, lxiii. p. 208), the value of  $\alpha$  for pure aluminium is  $10^{-8} [2204 + 2.12 t]$ , so that  $\beta = \cdot 000962$ . Hence, perhaps, until more decisive determinations are made in the case of pure zinc, by Mr. Tutton's improved interferometer method for instance, and as the molecular constitution of the metal is simple like that of copper and silver, we may take for  $\beta$  half the value deduced from Matthiessen's observations as in the case of most of the metals tabulated above.

From the values of  $\beta$  and  $\delta$  given above, we get the following results :

	$\beta'$ .	$\delta'$ .	$\frac{1}{2}(\beta' - \delta')$ .	$\alpha$ .	$\delta$ .
	$\cdot 00$	$\cdot 000$	$\cdot 000$	$\cdot 00$	$\cdot 00000$
Copper .....	1509	590	460	4125	167
Silver.....	0908	393	245	3910	090
Tin.....	2163	700	731	4396	270
Cadmium .....	1327	468	431	4096	168
Lead .....	0959	488	236	3901	087
Zinc .....	0966	533	217	3882	080
Aluminium .....	1206	478	364	4029	133

For magnesium  $\beta$  appears to be abnormally high. Thus, according to Fizeau, the value of  $\alpha$  at  $40^\circ$  is  $\cdot 00002694$ , and  $\cdot 00002762$  at  $50^\circ$ , so that  $\beta = \cdot 00281$ . We must therefore conclude, either that magnesium does not conform with the relation for  $\gamma$ , or that Fizeau's value for  $\beta$  is not characteristic of the metal itself, but of a particular specimen only. For the remaining metals, with the exception of those afterwards to be mentioned, data cannot be obtained respecting  $\delta$  and  $\beta$ .

According to the temperature relation  $\frac{\sigma}{\sigma_0} = 1 + [\epsilon + \frac{1}{2}(\beta' - \delta')]t + \frac{1}{2}\epsilon(\beta' - \delta')t^2$ , since in the case of the metals tabulated above  $\delta'$  is less than  $\beta'$ , the locus of  $u$  or  $\frac{\sigma}{\sigma_0}$  must be concave upwards, and the value of  $\frac{du}{dt}$  must increase as the temperature rises. This is in accord with the results of observation as the following table will show, where  $\frac{du}{dt}$  and its mean value between  $0^\circ$  and  $100^\circ$  are tabulated. For comparison, the

		$\frac{du}{dt}$	Mean.
Tin .....	T	$\cdot 00440 + \cdot 0000054 t$	$\cdot 00467$
	F	$\cdot 00425 + \cdot 0000040 t$	$\cdot 00445$
	B	$\cdot 00403 + \cdot 0000117 t$	$\cdot 00461$
Copper .....	T	$\cdot 00413 + \cdot 0000038 t$	$\cdot 00429$
	F	$\cdot 00412 + \cdot 0000033 t$	$\cdot 00428$
	E	$\cdot 00412 + \cdot 0000060 t$	$\cdot 00442$
Cadmium .....	T	$\cdot 00410 + \cdot 0000032 t$	$\cdot 00425$
	F	$\cdot 00405 + \cdot 0000028 t$	$\cdot 00419$
	V	$\cdot 00402 + \cdot 0000018 t$	$\cdot 00412$
Lead .....	T	$\cdot 00390 + \cdot 0000017 t$	$\cdot 00399$
	F	$\cdot 00399 + \cdot 0000028 t$	$\cdot 00411$
	B	$\cdot 00395 + \cdot 0000028 t$	$\cdot 00402$
Zinc .....	T	$\cdot 00388 + \cdot 0000016 t$	$\cdot 00396$
	F	$\cdot 00395 + \cdot 0000020 t$	$\cdot 00405$
Silver .....	T	$\cdot 00391 + \cdot 0000018 t$	$\cdot 00400$
	F	$\cdot 00391 + \cdot 0000018 t$	$\cdot 00400$
	B	$\cdot 00397 + \cdot 0000014 t$	$\cdot 00404$
Aluminium .....	T	$\cdot 00403 + \cdot 0000027 t$	$\cdot 00416$
	F	$\cdot 00408 + \cdot 0000030 t$	$\cdot 00423$
	B	$\cdot 00388 + \cdot 0000026 t$	$\cdot 00401$

values deduced from Fleming and Dewar's observations, denoted by F, those given by Benoit denoted by B, and those given by Vicentini and Omadei denoted by V, have also been inserted. The values calculated from Fleming and Dewar's observations have been obtained by applying to them the approximate relation  $\frac{\sigma}{\sigma_0} = (1 + \epsilon t)(1 + \gamma t)$  between  $0^\circ$  and  $100^\circ$ .

T denotes the values obtained from thermal data,  $\delta$  and  $\beta$ , while E, in the case of copper, denotes the values given by Elmore.

In the case of the metals tabulated above, it will be found that not only is  $\gamma$  approximately  $\frac{1}{2}(\beta' - \delta)$  and  $a$  approximately  $\epsilon + \frac{1}{2}(\beta' - \delta)$ , but that  $\gamma$  is also approximately  $\frac{1}{3}\beta$  or  $\frac{1}{3}\beta'$ , and  $a$  approximately  $\epsilon + \frac{1}{3}\beta'$ , or  $\epsilon + \frac{1}{3}\beta$ , as the table opposite (p. 209) will show.

In the table the column headed  $\gamma$  contains the values calculated for that constant from Fleming and Dewar's observations; the third column headed Diff. indicates the percentage difference of  $\frac{3\gamma}{\beta}$  from its mean value 1.046, while the second is the percentage difference of  $\frac{3\gamma}{\beta'}$  from its mean value .896.

From the table it will be seen that the order in which the metals stand as regards the values of  $\gamma$  is, with the exception of aluminium, the same as that as regards the values of  $\frac{1}{3}\beta$  and  $\frac{1}{3}\beta'$ ; that the ratios  $\frac{3\gamma}{\beta}$  and  $\frac{3\gamma}{\beta'}$  are approximately constant; and that the values deduced for  $a$  from  $\gamma$ , namely  $\epsilon + \gamma$ , are practically the same as those deduced from  $\beta$  and  $\beta'$ , namely  $\epsilon + \frac{1}{3}\beta$ , and  $\epsilon + \frac{1}{3}\beta'$ .

Hence, since for these metals  $\gamma$  is approximately  $\frac{1}{2}(\beta' - \delta)$ , and also approximately  $\frac{1}{3}\beta$  or  $\frac{1}{3}\beta'$ , it follows that  $\delta$  must be approximately  $\frac{1}{3}\beta'$ , and  $\delta$  approximately  $\frac{1}{3}\beta$ . That is, that the temperature-variation of the specific heat must depend upon that of the thermal expansibility, or, more correctly perhaps, that *the temperature-variation of the specific heat and that of the thermal expansibility must depend upon the temperature-variation of the same physical property of the metal.* This result, again, on account of uncertainties respecting the



<i>Metal.</i>	$\gamma$ . -000	$\frac{1}{\beta}$ . -000	$\frac{1}{\beta'}$ . -000	$\frac{3\gamma}{\beta}$ .	Diff. Per cent.	$\frac{3\gamma}{\beta'}$ .	Diff. Per cent.	$e+\gamma$ . -00	$e+\frac{1}{\beta}$ . -00	$e+\frac{1}{\beta'}$ . -00
Tin.....	538	557	721	.97	7.3	.75	16.3	4203	4222	4386
Copper ....	450	417	503	1.08	3.2	.9	.5	4115	4082	4168
Cadmium ..	384	375	443	1.02	2.5	.87	2.8	4049	4040	4108
Lead .....	326	283	320	1.15	10.0	1.02	13.8	3991	3943	3985
Zinc .....	289	283	320	1.02	2.5	.9	.5	3954	3948	3985
Silver .....	245	269	302	.89	14.5	.81	9.6	3910	3934	3967
Aluminium..	412	345	403	1.19	13.8	1.02	13.8	4077	4010	4070

experimental data bearing upon it, cannot be accepted without considerable doubt and hesitation. I have only ventured to put it forward because it appears to have enough probability in its favour, and to be sufficiently interesting and suggestive to deserve a fuller consideration, and to have a special investigation into the experimental facts bearing upon it made by competent observers.

If  $\epsilon$  is the average increase of  $s$  per unit rise of temperature, and if  $\delta = \frac{1}{3}\beta$ , as suggested above, then, approximately,  $\epsilon = \frac{1}{3}(s_0\beta) = \frac{2 \cdot 1\beta}{w}$ , where  $w$  is the atomic weight. The following are some of the results obtained for  $\epsilon$  from this relation:—

	$\beta$ °C	$w$ .	$\epsilon$ (calc.) °C	$\epsilon$ (obs.) °C	
Aluminium .....	1036	27	800	950	Naccari.
				1000	Richards.
Copper .....	1251	63.3	410	460	Bède.
				490	Trowbridge.
Tin .....	1671	119	295	341	Lorenz.
Cadmium .....	1124	112	210	240	Naccari.
Palladium .....	0880	106	175	210	Violle.
Silver .....	0806	108	160	210	Naccari.
Iridium .....	1198	192.5	131	151	Violle.
Platinum .....	0923	195	100	112	Violle.

The relation does not hold for the metals of the Iron group. Also, for many of the metals experimental results cannot be obtained to test the matter, while for metals like lead, magnesium, and zinc, the results available are not conclusive.

According to the relation  $\sigma \propto \frac{\theta}{q}$ , since  $\theta$  is constant during fusion, the change of resistance that accompanies fusion must depend upon the change in the value of  $q$ \*. Hence, if  $\sigma_s$  is the value of  $\sigma$  in the solid state just before fusion has begun, and  $\sigma_l$  its value in the liquid state just when fusion is completed, and if  $q_s$  and  $q_l$  be the corresponding values of  $q$ ,

\* Which implies that the average velocity of translation  $u$  of the moving electrons is not affected by the act of fusion, but remains unaltered like the temperature.

$\frac{\sigma_s}{\sigma_l} = \frac{q_s}{q_l}$ . For copper, silver, magnesium, zinc, cadmium, calcium, thallium, lead, and mercury,  $q \propto \frac{nh}{m\lambda}$ . If we assume that  $h$  in this relation is to stand for the *internal*, and not for the *total* energy of the atom, it will be the same in the solid and liquid states at the temperature of fusion. Hence, if  $\lambda_s, \lambda_l$  be the values of  $\lambda$  corresponding to  $\sigma_s, \sigma_l$ ,  $\frac{\sigma_s}{\sigma_l} = \frac{\lambda_s}{\lambda_l}$ .\*

The ratio  $\frac{\lambda_s}{\lambda_l}$  can be calculated from the increase of volume that accompanies the fusion. Thus, if  $d$  is the average distance between the centres of two neighbouring atoms at the absolute zero,  $d + \lambda_s$  and  $d + \lambda_l$  will be its values in the liquid and solid states respectively at the temperature of fusion. Also, if  $\rho_s$  and  $\rho_l$  be the corresponding densities, and if  $\left(\frac{\rho_s}{\rho_l}\right)^{\frac{1}{3}}$  or  $\frac{d + \lambda_s}{d + \lambda_l}$  be denoted by  $x$ , we get

$$\lambda_s = (d + \lambda_l)x - d.$$

Now the only cases where reliable information respecting  $\rho_s, \rho_l, \sigma_s$ , and  $\sigma_l$  can at present be obtained, are those of lead, cadmium, tin, and zinc, and in the case of these metals, since the melting-point is low, the average value of  $\alpha$  between  $0^\circ$  and  $100^\circ$  is probably not far from its value between absolute zero and the melting-point  $T$ , so that very approximately  $\lambda_s = d\alpha T$ . Hence

$$\frac{\lambda_s}{\lambda_l} = \frac{(1 + \alpha T)x - 1}{\alpha T},$$

the ratio being thus independent of the actual value of  $d$ . In order, however, to compare the value of  $\lambda_s$  with the constant of Pictet's law, namely  $V^{\frac{1}{3}}\alpha T$ , we shall put  $d = V^{\frac{1}{3}}$ .

The increase of volume that accompanies fusion has been specially investigated for several metals by Vicentini and Omadei, their results being taken in the table that follows except in the case of zinc.

\* This assumption implies that the electronization per unit volume, so far as it depends upon temperature, is determined:—

(1) By the kinetic energy of an atom considered as a system of electrons in orbital motion,—this being unaffected by fusion, since the temperature of the atom is not altered.

(2) By the average distance apart of the atomic centres,—which is directly affected by fusion.

	$\rho_s$	$\rho_l$	$\lambda_s$	$\lambda_l$	$\frac{\lambda_s}{\lambda_l}$	$\frac{\sigma_s}{\sigma_l}$	Diff.
Lead .....	11.005	10.645	.076	.046	1.66	1.9	+12 p. cent.
Cadmium ...	8.366	7.989	.085	.044	1.93	2.3	+16 "
Tin .....	7.183	6.968	.064	.029	1.86	2.1	+12 "
Zinc .....	.....	6.480	.067	.042	2.07	2.0	- 4 "

Vassura's values for  $\frac{\sigma_s}{\sigma_l}$  have been taken in the case of cadmium and tin, and De la Rive's in the case of lead and zinc.

Omadei gives no values for  $\rho_s$  and  $\rho_l$  in the case of zinc. According to Roberts-Austen, however, the density of zinc just when fusion is completed is 6.480, from which value  $\frac{\lambda_s}{\lambda_l}$  can be calculated.

Taking the results in the table as experimentally valid, it is seen that to a rough approximation  $\frac{\sigma_s}{\sigma_l} = \frac{\lambda_s}{\lambda_l}$ . The determination of  $\frac{\lambda_s}{\lambda_l}$ , however, is a matter of difficulty, the results obtained above from  $\frac{\rho_s}{\rho_l}$  being undoubtedly imperfect and unreliable. Thus, Omadei's value for the percentage increase of volume of thallium in the act of fusion is 4.32, whereas, according to Toepler, it ought to be 3.22. The former of these values gives  $\lambda_s = .081$  and  $\frac{\lambda_s}{\lambda_l} = 1.84$ , whereas the latter gives  $\lambda_s = .072$ , and  $\frac{\lambda_s}{\lambda_l} = 1.64$ . Moreover, it is not probable that the increase of resistance that accompanies fusion is determined by the increase in  $\lambda$  alone, though possibly  $\lambda$  may be the most important factor concerned in the matter. At any rate it is worthy of note that, whereas in the case of metals which expand on melting the specific resistance is greater in the liquid than in the solid state at the temperature of fusion, in the case of bismuth and antimony, which contract on melting, it is less.

Platinum and palladium differ from the metals already discussed, as regards their temperature-coefficients, in the fact that for them the value of  $\alpha$  is less than  $\frac{1}{273}$ , and the locus

of  $\sigma$  concave towards the axis of temperature, whereas, in the case of the other and apparently simpler metals,  $\alpha$  is greater than  $\frac{1}{273}$  and the locus of  $\sigma$  convex towards that axis. This anomaly indicates that for platinum and palladium, the temperature-variation of the electronization-coefficient  $q$  cannot be accounted for by the temperature-variations of  $\lambda$  and  $h$ , as in the case of the simpler metals. Some other factor has to be superposed upon these in order to convert into an increase the decrease that would arise in  $q$  from them alone. The thermoelectric curves of platinum and palladium are also exceptional as compared to those of the simpler metals. For whereas the curves, as given by Fleming and Dewar, have a positive curvature for the simpler metals, for platinum and palladium the curvature is decidedly negative. These exceptional characteristics are probably closely related, since on the electronic theory both the electrical resistance and the thermoelectric properties of a metal depend upon the electronization-coefficient  $q$ .

As might be expected from their ferro-magnetic properties, iron, nickel, and cobalt, as regards their temperature-coefficients, constitute an exceptional and highly characteristic group, the discussion of which must be reserved for a future occasion.

The results discussed in the paper may be summarized thus :—

(1) A relation  $\sigma = \frac{KmV\theta}{eT}$  which roughly holds for

Silver,	Platinum,
Copper,	Palladium,
Magnesium,	Thallium,
Sodium,	Lead,
Zinc,	Mercury,
Cadmium,	Arsenic,
Calcium,	Antimony,
Potassium,	Bismuth ;

but fails for gold, indium, tin, and aluminium. It also fails, as we should expect, for iron, nickel, and cobalt—while in the case of the remaining metals data cannot be obtained to test the matter.

(2) A temperature factor

$$\frac{\sigma}{\sigma_0} = (1 + \epsilon t) \left[ 1 + \frac{1}{2} (\beta' - \delta') t + \dots \right]$$

obtained from the relation  $q \propto \frac{nh}{m\lambda}$ , approximately true for tin, copper, cadmium, lead, zinc, silver, and aluminium, but not for platinum and palladium, and of course the metals of the Iron group.

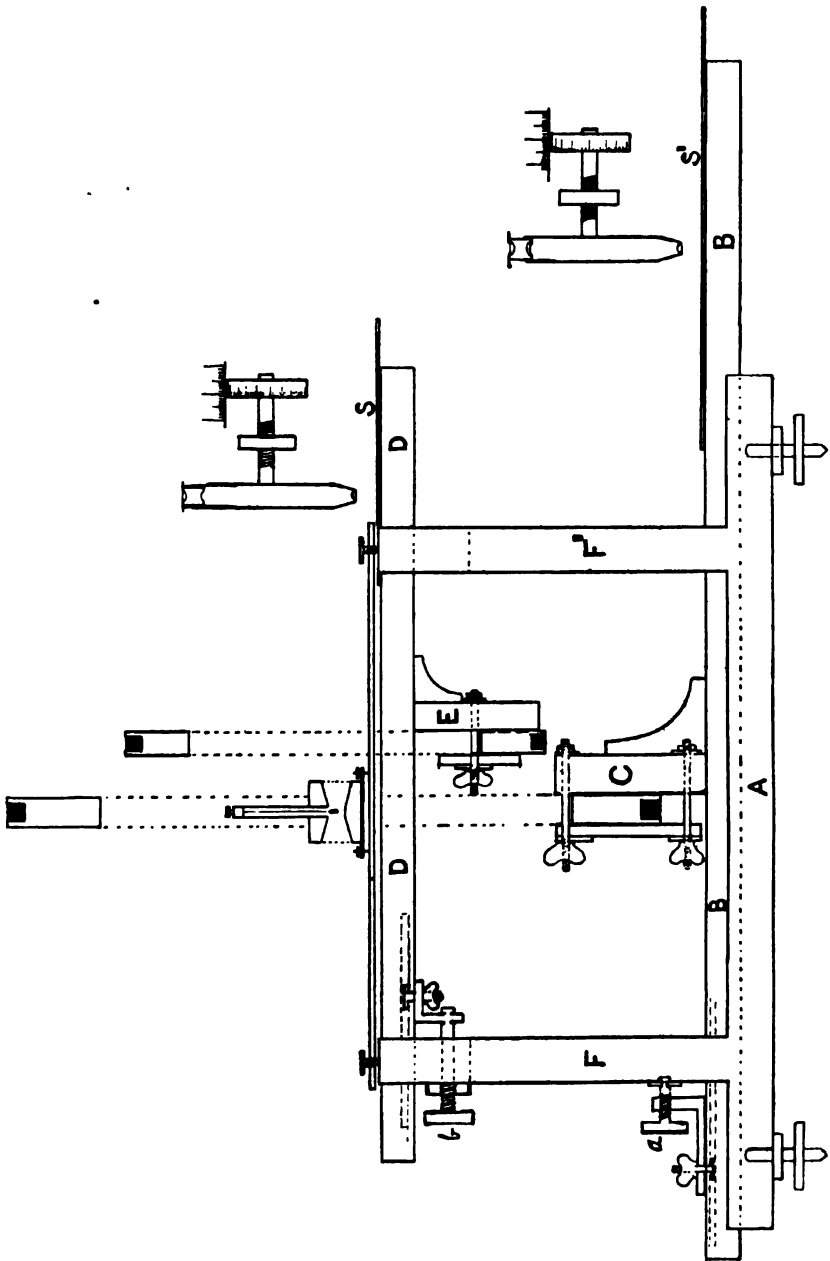
(3) A specific heat relation  $\epsilon = \frac{2.1\beta}{w}$ , approximately true for

Aluminium,  
Copper,  
Tin,  
Cadmium,  
Palladium,  
Silver,  
Iridium,  
Platinum ;

but not, of course, for the metals of the Iron group. The results are uncertain in the case of lead, magnesium, and zinc; while in the case of the remaining metals, the relation cannot at present be tested.

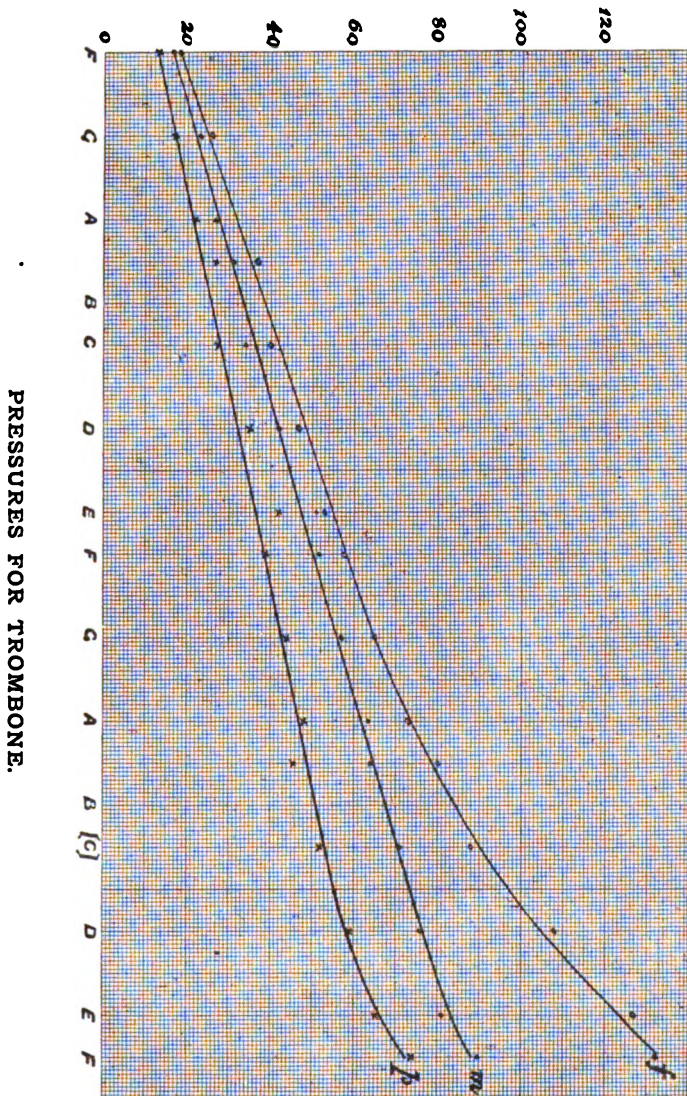
(4) A relation  $\frac{\sigma_s}{\sigma_i} = \frac{\lambda_s}{\lambda_i}$  at the temperature of fusion, roughly true for lead, cadmium, tin, and zinc, the only metals for which, at present, it can be tested.

The results, however, in many respects are incomplete and unsatisfactory, as of course is to be expected from the imperfect character of their experimental basis. Perhaps, however, the paper—in spite of its imperfections, may prove useful as a statement of what may be done to correlate expansion-coefficients, specific heats, and electrical resistances, and that it may do good by calling attention to the matter, and stimulating experienced observers to take up its systematic investigation.

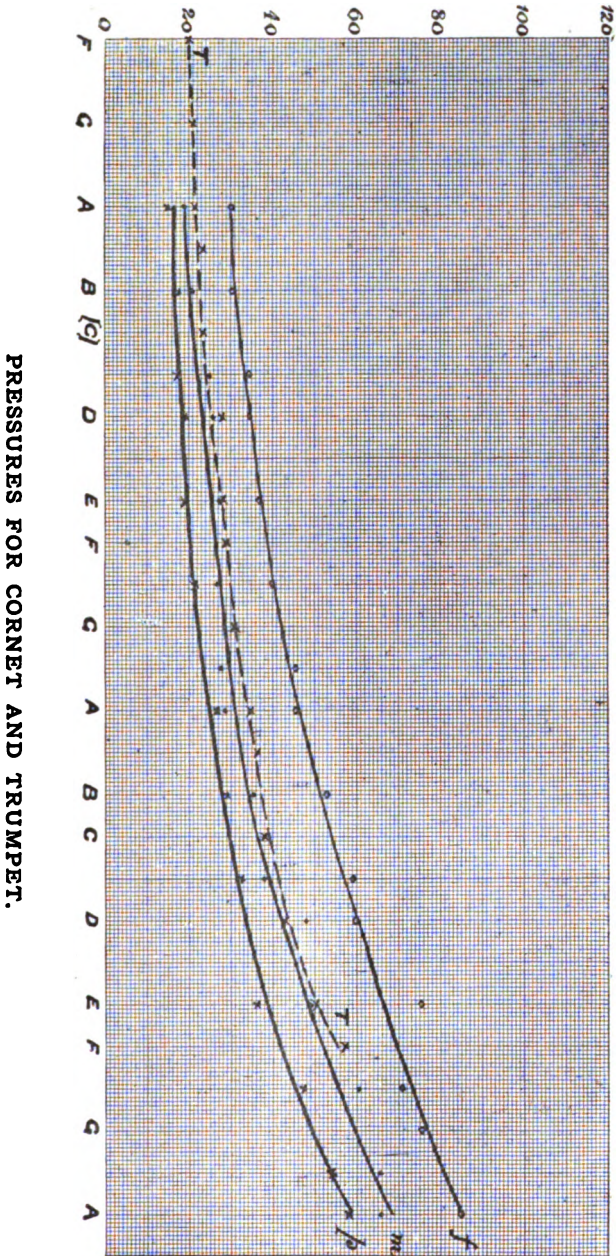












PRESSURES FOR CORNET AND TRUMPET.



## ADDRESS OF THE PRESIDENT.

Professor SILVANUS P. THOMPSON, D.Sc., F.R.S.

*Delivered at the Annual General Meeting,  
February 14th, 1902.*

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IN the year which has passed since I had the honour of addressing you from this Chair, some changes, happily few, have passed over the membership of our Society. Death has, however, robbed us of two of our Honorary Fellows, and it is fitting that we should pay at least a passing tribute to their worth.

Professor HENRY A. ROWLAND, who had been our Honorary Member since 1884, died suddenly on April 16th, 1901, aged 53 years. He was educated as an engineer, and graduated in 1870 at the Rensselaer Polytechnic at Troy, N.Y. He subsequently joined the staff of that College as Assistant Professor, and on the founding of Johns Hopkins University at Baltimore, was appointed its Professor of Physics. Prior to this, he had made researches on the magnetic permeability of iron, using the ring method, which he perfected greatly. This research was published through the intermediation of Clerk Maxwell in the *Philosophical Magazine*. Prior to taking up his Chair at Baltimore, he spent a year in Berlin in the laboratory of Helmholtz, where he carried out the classical experiment of measuring the magnetic field due to the rotation of a charged disc of ebonite. Though some doubt was thrown upon this experiment by Lecher some years ago, and by Crémieu more recently, there seems to be no doubt that in such experiments electric convection does produce a magnetic field in accordance with the conceptions of Faraday and Maxwell. After Lecher's unsuccessful attempt of 1885 to repeat the experiment, I urged upon Rowland that he should himself repeat it under better conditions than those possible in 1875. This he did in collaboration with Dr. Hutchinson; the results being published in 1889. Rowland's career at Baltimore was fruitful in original researches of great precision. He determined and redetermined the absolute value of the B.A. unit of resistance, using a modification of the method of Kirchhoff. He

also redetermined the absolute value of the specific heat of water, commonly called Joule's equivalent, using an apparatus on the same principle as Joule's perfected apparatus of 1898, but on a larger scale, requiring an engine to drive it, and converting much more energy into heat in a given time than had been possible in the older determinations. Rowland's value ranks amongst the most accurate of the determinations of "J." In 1882, he communicated to this Society an account of the concave diffraction-grating, by which it became possible to produce spectrum photographs directly, without the intervention of lenses or prisms. To perfect the grating he devoted himself with untiring energy, and himself designed a new ruling machine which was set up in the basement of his laboratory at Baltimore. The fruitfulness of this instrument of research in his hands and in the hands of others is too well known to need any comment. Rowland's own large-scale maps of the spectrum, photographed by its means, are a witness to its capability. He also with it investigated the wave-lengths of the principal spectrum-lines. His Table of standard wave-lengths, published in the *Philosophical Magazine* for July 1893, remains of permanent authority. At the Electrical Exhibition of 1884 at Philadelphia he presided at the Congress of Electricians, and read a paper on dynamos in which he enunciated the principle of the magnetic circuit. He occupied himself during recent years with multiplex telegraphy and some other practical applications of electricity; but his heart was in more abstract researches, and by these he will be known. He presided at the International Congress of Electricity at Chicago in 1893, and was a permanent member of the International Commission on Standards. He was the first President of the American Physical Society. He was elected a Foreign Member of the Royal Society in 1889.

Dr. RUDOLPH KOENIG, the eminent constructor of acoustical instruments, the inventor of the ingenious manometric flame so useful in acoustic research, and the author of many important experimental researches in acoustics, died October 2nd, 1901, aged 68. He was elected as our Honorary Fellow only at the last Annual General Meeting. To his scientific work I made a lengthy allusion in my Presidential Address of last year. There is little now to add, save to recall with a mournful satisfaction that in his failing condition of health, he received with undisguised pleasure the recognition of his services to physical science implied in our Honorary Fellowship.

He left behind an unpublished memoir, sufficiently completed, I trust, for publication, relating to the influence of the phase of the components of a compound tone upon its timbre. He had devised some new experiments which he himself showed me in September 1900; having been enabled, as he told me with a feeble smile, to afford the cost of the new apparatus, because in the spring his business had been somewhat more prosperous than of late. At the time of his death the great Tonometer was still in his possession. Would that this incomparable collection of acoustical standards—unique as it must for ever be—could be purchased, ere too late, for our National Collection. Such a collection, whatever its destination, ought not to be dispersed. Its preservation intact as a monument of the great acoustician will be desired by every lover of physical science.

You have this day chosen to fill the gaps in the rank of our Honorary Fellows the names of Professor Samuel Pierpont Langley and of Professor Hendrik Antoon Lorentz.

Professor **LANGLEY** needs no words from me to commend him to you. You are aware of the eminent position which he holds in the United States as Director of the Smithsonian Institution of Washington; and all the world knows of the admirable work which he did while Director of the Alleghany Observatory. In his book, published in 1884 by the United States Signal Service, under the title of *Researches in Solar Heat and its Absorption by the Earth's Atmosphere*, Langley put together a large number of facts and observations which had in part been previously announced in his original memoirs. For some time, his observations of solar radiation were made with black-bulb thermometers, with the actinometer, and the pyrheliometer. But, not satisfied with these instruments, he devised the bolometer, an apparatus which, since it depends upon the change of electric resistance produced in a thin conductor of blackened metal, and observed electrically, can readily be made into a recording instrument. In Langley's hands it became a sufficiently sensitive instrument to be capable of application to spectroscopic work. It is, in fact, with the spectro-bolometer that the greater part of Langley's later work has been accomplished. Armed with this instrument of research, he has explored in the clear air of the high North-American peaks, the infra-red region of the spectrum, known to us it is true to a limited extent before. Sir William Herschel in 1880 had found that a thermometer placed in the



spectrum showed heating effects beyond the limit of the visible radiations at the red end; while his son Sir John Herschel, in 1840 published a crude thermograph showing discontinuous absorption in that region. Tyndall in 1866 concluded that about one-third only of the energy radiated is comprised within the visible spectrum; the remaining two-thirds being in the infra-red. In 1876 Edmond Becquerel, using a phosphorescent method discovered by him in 1842, had roughly mapped the infra-red spectrum; while his son Henri Becquerel in 1883 carried out this mapping much further, using a bisulphide prism and a Rutherford grating. Our former President, Sir William Abney, taking advantage of his own discovery of the sensitiveness of bromide of silver emulsions to red and infra-red light, produced in 1886, after several years of work, a map of the infra-red region from the line A down to a wave-length of about 180 microcentimetres, with a table of over 400 absorption-lines. This map he had photographed by means of a Rowland concave grating. But Langley has now extended the limits of our knowledge. In his researches from 1891 to 1898, he has investigated what may be called the "lower infra-red region" down to a wave-length of over 530 microcentimetres; so that the now known infra-red spectrum extends to a length more than ten times that of the visible spectrum. In his recent book, *Annals of the Astrophysical Observatory of the Smithsonian Institution* (Washington, 1900), he gives a magnificent map of this region of the spectrum, as taken by the bolometer with a rock-salt prism of 60°. He finds well-defined absorption-bands and lines, many of which are due to terrestrial atmospheric absorption, some of them showing an annual variation of definite regularity, others liable to irregular change. He has thus opened out a new chapter connecting meteorology with the properties of the infra-red rays. Professor Langley is well-known personally to many physicists on our side of the Atlantic: he was elected a Foreign Member of the Royal Society in 1895. But in view of his recent achievements, we may well feel that we may congratulate ourselves on being permitted to enroll him now amongst our twelve Honorary Fellows.

Professor HENDRIK ANTOON LORENTZ has made for himself a name in a very different branch of physics, that of mathematical theory, which he has applied with great elegance to the problem of the aberration of light, to the equations of the electromagnetic field, and to the theory of electrons. The greater part of his contribution to



physics is to be found in papers which have appeared during the past twenty-five years in the *Archives Néerlandaises*.

He has worked at hydrodynamics, sound, and thermodynamics, but his most important work is without doubt his extension of the theory of Maxwell, by the introduction of new conceptions in relation to the interaction of ponderable matter and imponderable ether. It is familiar history that though Maxwell's work was followed up and very generally accepted by British physicists during his life-time and in the years which immediately followed, it was not till ten years later, when Hertz's researches established experimentally the phenomena of the electromagnetic waves, that Continental physicists generally began to appreciate its merits. Long before this, however, Maxwell's work had been assiduously studied in Holland. Lorentz's thesis for the doctorate, in 1875, shows a deep understanding of it. In this paper he explains the electromagnetic theory of the refraction and reflexion of light; having been led to this study by an assertion of Helmholtz that the formulæ of Fresnel could be explained by the electromagnetic theory of light better than by any other form of the undulatory theory. Lorentz, indeed, brought in evidence that Maxwell's theory is to be preferred to the other theories. This result he derived not only from the calculation of ordinary reflexion and refraction, but also from an investigation of total-reflexion, crystalline reflexion, and metallic reflexion. At the end of the same paper, he points out that dispersion and emission have also to be brought under this theory. This extension, including also aberration, Lorentz published twenty years later, in 1895, in his *Theorie der elektrischen und optischen Erscheinungen in bewegten Körpern*, being a recast of another paper of 1892, entitled *la Théorie électromagnétique de Maxwell et son application aux corps mouvants*, this being again a development of a communication to the Academy of Amsterdam in 1891, and showing that all electrodynamic phenomena can be explained by applying the electromagnetic equations for moving conductors to moving atoms of electricity. Lorentz's conception of the relation between matter and ether is condensed in this paper into a simple mathematical formula including the laws of all electric and optical phenomena. The stepping-stones by which he arrived at this conception, a conception wide enough to eliminate any special hypothesis as to the structure of matter, yet definite enough to allow rigorous mathematical treatment, were the following. In 1878, following closely upon his thesis for the doctorate, he investigated the relation

between density and refractivity, and so, independently of Lorenz of Copenhagen, discovered the law  $\frac{(n^2 - 1)}{(n^2 + 1)d} = \text{constant}$ . To obtain this result he was obliged to take into consideration more strictly than before the molecular structure of the ponderable medium, and to accept the possibility that in every molecule there are particles with opposite charges of which one kind can shift under the influence of external forces; the surrounding ether being supposed to have the same properties as *in vacuo*. The explanation of dispersion was then given by assuming that the electric particles, shifted to a certain extent by elastic forces against a harmonic force exerted by the ponderable atoms, have a certain mass. In Lorentz's memoir on the formulæ of electrodynamics, published in 1891, there is nothing pointing to a further use of electric particles for explaining electrodynamic laws: even in his paper of 1883, on the explanation of the Kerr effect and allied magneto-optic effects, by postulating a Hall effect on the electric-light vibration-currents, he does not recur to the conception of electric particles which later he used to such striking purpose. The starting-point from which Lorentz travelled toward the new views on the rôle of the ions was the study of the intricate problem of aberration. Those new views he reached only after a struggle of some years with the difficulties presented by the aberration-theory of Stokes, and the experiment of Michelson. In his memoir entitled *De l'influence du mouvement de la terre sur les phénomènes lumineux*, which appeared in the *Archives* in 1887 (vol. xxi. pp. 103-176), he discusses with great keenness the experiments of Michelson in relation to the theories of Fresnel and of Stokes, and concludes that so far as the facts of Michelson's observations are concerned, they lend support to Stokes's supposition that the ether moves in independence of the matter of the earth. The exceeding difficulties of discussions of this sort suffice to bring out the real genius of the man. It would be of interest to know Lorentz's views on the recent work in this direction of Prof. Lodge, and the still more recent and rather surprising paper of Professor Hicks.

In Lorentz's paper of 1892 on Maxwell's electromagnetic theory and its application to moving bodies, he starts with the postulates of Maxwell's theory and compares them with those of Hertz. He points out the distinction between the methods pursued by these two great thinkers: Maxwell always haunted by his mechanical analogies and attempting to explain the properties of the electro-

magnetic field by the properties such as inertia and momentum of mechanical systems; Hertz, on the other hand, contenting himself with clear and succinct descriptions, independent of all preconceived ideas as to that which passes in the electromagnetic field. Lorentz appears to sympathize with both methods of vision; and in attempting to generalize Maxwell's methods was clearly influenced by Hertz's views. But his principal aim in this generalization was to ascertain the laws which would govern the movement of electricity in bodies which should in their movement in space not drag the ether (as Hertz had assumed) along with them. Adopting the displacements or movements of the ions as the causes of electric phenomena, he extends Maxwell's fundamental equations to include their movements. To attempt here to give any outline even of these memoirs of Lorentz would be misplaced labour. Suffice it to say that, amongst a number of other results, he arrives at the conclusion that the movement of ponderable matter impresses on ether waves a velocity which is a determinate fraction of its own, the factor being precisely the coefficient introduced arbitrarily by Fresnel into the theory of aberration.

In the memoir mentioned, and in others which followed it, Lorentz took up in a refined form his earlier hypothesis, and proceeded to apply the theory of a system of electric particles moving through the ether, leaving the ether itself at rest. In this theory the electric corpuscles are now clearly and explicitly named; and, in harmony with the views of Giese, Schuster, Arrhenius, Elster and Geitel, they are provisionally identified with the ions of electrolysis. Formulæ are now given in the style of Maxwell for the state of the ether in the neighbourhood of the electric particles and for the forces exerted by the ether on the corpuscles. Looking at these formulæ, one sees at a glance that in every experiment where a conductor is displaced, in order to understand the true meaning of the resulting phenomena one must go back to the whole discussion that is at the bottom of the aberration theory. The theory of Lorentz partakes of the old form of that of Weber and Clausius as well as of that of Maxwell. Electrostatics return mathematically to the old form of Coulomb; but the electrical interactions are propagated through the ether, as in Maxwell's theory; and in optics the equations yield Fresnel's coefficient for aberration phenomena. An opportunity to test the new theory experimentally presented itself within a very few years of its publication. While pursuing another train of ideas, and one which had occurred to him during a

protracted research on the Kerr effect, Zeeman discovered that the magnet exercises an influence on the light emitted or absorbed by metallic vapours. Lorentz immediately realized the important bearing which this new fact had upon his theory. The explanation of the fact which his theory was able to afford was so striking, that it has been universally accepted as a direct proof of the fundamental correctness of the theory. And not only did Lorentz give the explanation of the Zeeman effect, but he added a brilliant prediction as to the polarization of the doublets and triplets which Zeeman had found in the spectral lines. This polarization was verified immediately by Zeeman, thus leaving no doubt as to the nature of the new effect. In the mean time Lorentz, showing how the mass of the "light-ions" could be determined from the observations of Zeeman, that is to say from optical phenomena, found in Zeeman's discovery the means of putting the finishing touch to his theory, inasmuch as it enabled him to identify these "light-ions" with the electrons introduced in other departments of research.

Many important contributions to the theory of magneto-optic phenomena have since been given by Lorentz. He has given a *résumé* of them in the Report which he presented to the Congress of Physics at Paris in 1900. He has also applied his views to furnish a hypothesis to explain the null result of the famous Michelson-Morley experiment, viz., that the dimensions of a body are subjected to a minute change by their translation through the ether. He has also investigated a kindred explanation of gravitation. He deduced from the law of Wien the inference that the electrons in all bodies are of the same size. To sum up all this admirable work, it may suffice to say that to Lorentz we owe the new proof derived from optics of the necessity of recasting our fundamental ideas in physics in the way that this reconstruction has already been forced upon us in electrical matters, the essence of that new fundamental idea being that which Lord Kelvin has so recently discussed under the title of "Aepinus atomized," that new atomic theory of electricity which has emerged from the work of Faraday, Hittorf, Helmholtz, Budde, Stoney, Arrhenius, and J. J. Thomson.

Very important work has also been done by Lorentz in the kinetic theory of gases. In 1880 he deduced from Boltzmann's differential equation for the law of molecular velocities in a medium where the densities and velocities of the gas are not everywhere the same, a law for the propagation of sound in a gas. In 1887 he attacked the law of partition of velocities, and treating the problem

of the reversal of molecular collisions as set forth by Boltzmann, he devised a new and simpler proof of Maxwell's velocity-partition law for monatomic gases, and removed some of the difficulties in finding the relation between the differentials of variables characterizing the beginning and end of a molecular collision. He also published a study on the meaning of the laws of emission proposed by Boltzmann and by Wien. In 1881, in a contribution to the study of the equations of state, he described a mode of finding the correction for the volume of the molecules in van der Waals's theory, by calculating the virial of the impulses of the collisions, a method later developed by Boltzmann in his treatise on the kinetic theory of gases. To this, in 1891, he added some considerations on the kinetic theory of solutions, and in 1897 some applications of the thermodynamic potential in connexion with questions of equilibrium of phases occurring in Schreinmaker's extensive experimental research on equilibrium in ternary systems.

Lorentz has also published a very admirable series of papers in the *Physikalische Zeitschrift* on the electromagnetic theories of physical phenomena. His latest paper, published last November, is *upon the method of the revolving mirror for the determination of the velocity of light*. He discusses here the question whether, since the act of reflexion at the surface of a mirror must take a finite, though excessively short, time, the revolving mirror must not necessarily drag round the luminous beam with itself. He finds that no error from this source could affect the accepted value of the velocity of light by one ten-millionth part; and that if the perturbing effect of the revolving air, caught by the mirror, is taken into account, the error from that source would not exceed one part in twenty-five millions.

Lorentz is not only a pioneer in mathematical physics, he is above all one of the leaders of scientific life in Holland, a man of wide sympathies and views, one whom it is truly a privilege to enrol within our ranks\*.

During the course of last month one of our most distinguished Honorary Fellows, Professor Hittorf of Münster, completed the fiftieth year of his professoriate. On the 11th of January

\* In preparing this notice of Prof. H. A. Lorentz, I am indebted to Prof. H. Kammerlingk-Onnes, who has kindly furnished me with a complete Bibliography of the scientific memoirs of Lorentz, and copious Notes thereon.—S. P. T.

I addressed to him a brief telegram congratulating him in the name of the Physical Society of London on the attainment of his Jubilee. I have since received from Professor Hittorf a letter acknowledging the good wishes so conveyed to him, and asking me to communicate his best thanks to the Society.

The Fellows of the Society are probably aware that some years ago an organization was set on foot under the name of the Gilbert Club, the principal aim of which was to guarantee the cost of producing an English version of the great classical work of Dr. William Gilbert, the *De Magnete*, which was published in London in the year 1600.

The work of translation, revision, and production which was entrusted to a small committee of the Club took an unexpectedly long time. Amongst those who took part in the work in one way or another were the late Mr. Latimer Clark, F.R.S., the late Sir Benjamin W. Richardson, F.R.S., Dr. Joseph Larmor, Sec.R.S., Prof. R. A. Sampson, Mr. H. B. Wheatley, Mr. Conrad W. Cooke, Prof. Meldola, F.R.S., Rev. A. W. Howard, Rev. W. C. Howell, and myself. Our ideal was to produce the work as nearly in the same style as the original Latin folio—in fact as Gilbert would himself have produced it if he had written in English instead of Latin. We may have come short of that ideal, but we hope at least that the book in its new form is not unworthy of its celebrated author, the father of the science of electricity and of the theory of terrestrial magnetism. We had hoped that the work would have been completed in 1900, the three-hundredth year after its original publication. But though most of it was in type by the end of that year, and the title-page bears 1900 as its date, the printing of the later sheets was not completed before the summer of 1901. It comes about, therefore, that the work has been put into the hands of its subscribers during my year of office as your President, a circumstance which entitles me to mention it here; though obviously, as I have taken a leading part in the work of its production, it would be out of place for me to comment upon the merits of the book. With your kind permission I will place a copy upon the shelves of the Library of the Society. In this connexion I will merely say that a statue of Dr. Gilbert is shortly to be erected in one of the niches of the Town Hall of Colchester, his native place, and that it is intended to celebrate in his memory the Tercentenary of his death on November 3rd, 1903.

Occupied as our Society is with pure Science rather than with its applications, any reference to the protection of scientific inventions by patents might seem scarcely germane to a Presidential Address. The time has long gone by when a Scientific Society should take the arbitrary course of refusing a paper upon any topic which has been made the subject-matter of letters patent. Foolish as such an attitude toward the inventor was, it was, doubtless, intended to uphold the view that there is virtue in the pursuit of science for its own sake, apart from material rewards which its applications may bring. But what can be said for the counter-proposition, which is today unfortunately true, that the law refuses to recognize as valid matter for the granting of letters patent anything which may have been brought before any of the learned or scientific societies? In the abstract one would have thought that if any course of action would establish any man's right to receive credit for a scientific invention embodying some new discovery or the application of scientific principles to novel and useful applications, that course would be the reading of a paper on the subject before a body of qualified critics. For by so doing the author submits the subject to the test of public discussion by those most likely to understand its importance. But no: as the law stands, no man after having read a paper before any of the learned societies on any invention, however meritorious, can take out a valid patent for the same. It is not so in the United States: in that country a man may appeal to the fact of his having read such a paper in proof of his subsequent claim to receive a valid patent for his invention. The law in this country works very inequitably. As an example, the late Professor Hughes, in May 1878, described before the Royal Society his classical researches on the microphone. Thereby he debarred himself from taking out a patent for the same. But, unfortunately, his benevolent intention of making his invention a present to the scientific world was defeated. There came after him a host of so-called inventors who took out patents for arranging two, four, six, or more Hughes's microphones in particular ways. One heard of Johnson's transmitter, of Cross'ey's transmitter, of Blake's transmitter, of the Gower transmitter, of Moseley's transmitter, all of which patents were sold for large sums of money: while Hughes the real inventor received nothing, not even the legal credit for his invention.

Let me mention a much smaller matter of quite recent occurrence. Many of the Fellows present will remember a meeting of this

Society on December 8th, 1890, when I read a paper on Cylindrical Lenses, such as are used for measuring and correcting astigmatism. I had worked out new formulæ for the refractive power of two such cylindrical lenses crossed obliquely; and while working at this investigation it occurred to me that it would be possible to devise an instrument, never before known, which would give a variable amount of cylindrical refraction along any given meridian. This I achieved by taking two cylindrical lenses, both of which had equal positive and negative curvatures respectively on their two faces (but with axes of cylindricity set at right-angles to one another). These I mounted one in front of the other so that they could be given equal angular movements in opposite directions. I had a little instrument made up—and it was exhibited at that meeting, publicly—with the two lenses arranged with a driving-pinion between their mounts, so that if one was rotated  $10^\circ$  to the right, the other would simultaneously be rotated  $10^\circ$  to the left. Now marked what happened. Less than two months after my publication before this Society of this invention a patent was taken out for this very same thing, and it is being now manufactured and sold under the name of Mr. ———'s Astigometer. I have no remedy. The fact that I showed the instrument before this Society does not in the eye of the law give me any prior right; at the most it invalidates the patent that was granted to the sharp-witted optician who has pirated my invention.

Take a third example, even more striking in its nature. In 1894 there was publicly described before two learned bodies, the Royal Institution and the British Association at its Oxford meeting, an account of the application of Hertz-waves to transmit signals to a distance. This was accomplished by using as receiver a coherer in a local circuit with a telegraph-instrument (a Morse receiver or an electric bell), and the coherer was made to decohere after each signal by tapping it either by hand or by a clock, or else by the vibrations of the telegraph-instrument. I was present on both occasions, and saw the signals so telegraphed without wires from one room to another, or, in the case at Oxford, from one building (the Clarendon Laboratory) to another (the University Museum). You all know that he who accomplished this feat, the true and original inventor of the so-called wireless telegraphy, was no other than my predecessor in this Chair, Principal Oliver Lodge. Now mark what has followed. Lodge having, as one would have thought,



established for ever by his thus seeking publicity and the criticism of his peers in science, by communicating his invention to bodies competent to judge, took out no British patent for his invention. Indeed, having so described it he cannot—as our foolish law stands—obtain a valid British patent for his invention. Two years go by, and the Government, through its Patent Office, is asked to grant a patent which on the face of it covers the use of a coherer in a local circuit, with telegraph-instruments and automatic tappers, for receiving Hertz-waves. Every one knows that this patent was granted to a certain Signor Marconi, who up to that date had done absolutely nothing that Lodge had not done before him. What remedy has Lodge? Nay, what remedy has the British public against being thus imposed upon? None save the indifferent satisfaction of knowing that a patent granted under such circumstances must, if called into legal question, prove invalid. But, strange as this injustice may seem, it is not more strange than the sequel, namely, that Lodge is in the United States, under its more enlightened patent laws, granted a patent that covers the system which he invented; and the irony of the situation is that in order to establish his claims to be accorded this American patent, he appeals to the dates of his lectures at the Royal Institution and at Oxford to prove his case!

Is it not time then that something was done to remedy this outrageous state of things in England? There is now before Parliament a Patent Law Amendment Bill. Why should not Parliament be asked to insert a clause which should have this effect: that publication by any scientific man before any of the recognized and scientific societies should be regarded as affording a *prima facie* claim to the invention therein described, and as evidence of the date of such claim? One of the provisions of the Bill is that what are known as “paper anticipations”—prior suggestions by other persons than the inventor, which never passed into fact or led to any result—should no longer, as hitherto, be regarded as reasons for upsetting an otherwise good patent. Surely if there is any kind of prior publication which ought to be excluded from operating to invalidate a patent, it is the inventor's own account to a scientific body of that which he has achieved. To turn it, as the law at present does, into a weapon of destruction against himself, is an injustice to the individual, and hurts the scientific societies, because it makes the scientific worker, who thinks he sees some useful

application looming ahead to reward him for his toil, hold back from making any communication to the scientific society, lest he damage in any way his prospective rights.

But lastly, it is not on the utilitarian applications of physics that I would dwell, since none of us knows what branch of the most abstract science may or may not bear within itself the germs of some future utilitarian application. When we see how by an unwritten law the useful application (so-called) reacts on the progress of pure science, we may well abstain from drawing invidious lines of demarcation. Was not the telephone answerable for almost all the attention given by the devotees of pure science between 1878 and 1888 to the subjects of self-induction and electric oscillations? Was not the telegraph, and especially the submarine telegraph, responsible for all our modern systems, instruments, and even theories of electrical measurement? Has not the need of practical improvement in telescopes and microscopes been at the bottom of all the advances in theoretical optics from the days of Newton and Euler to those of Abbe and of Lord Rayleigh? The work of Rowland and of Langley, can it be dissociated from that branch of practical optics which deals with the ruling of diffraction-gratings? Or, on the other hand, shall we think any the less of the study of the Kerr effect, or of the Zeeman effect, or of the Becquerel rays, because none of them has yet been worth sixpence from the utilitarian point of view? When Arago discovered that slices of quartz would rotate the plane of polarization of light, and, in concert with Biot, constructed the first rude instrument—polarimeter or polaristrobometer we may call it—to measure the amount of that rotation, no one, I imagine, dreamed that this discovery of pure science would become a matter worth millions a year to Great Britain, or of financial importance to her West Indian Colonies. And yet we know that the great beet-root sugar industry has grown up and almost ousted the industry in cane-sugar, mainly because of the possibility of using in the sugar factories the polarimeter to measure optically the strength of sugar solutions. The scientific discovery of today may, like the scientific theory of today, appear useless to the man in the street. But the most utilitarian practice of today is founded upon the apparently useless theory of yesterday, or upon the still more useless observation of the day before. Pure science, whether in observation of facts or in the

correlation of phenomena and their generalization into theory, goes on her way quite independent of eventual utilitarian applications. Only she looks to those who may have benefitted by the utilitarian applications to keep alive the torch and feed its flame. Within the membership of the Physical Society we number men who belong to each class of workers. To both we appeal that they will continue to support and to extend the usefulness of the Society, enabling it to band together for good all who desire to promote the advance of Physical Science in all its branches.

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XVI. *On the Measurement of Young's Modulus.* By W. CASSIE, M.A., *Professor of Physics in the Royal Holloway College* \*.

A RELIABLE oscillation method of measuring the stretch modulus ought to have advantages in accuracy and convenience which would give it some practical value. A method depending upon the oscillations of a spiral spring has been given by Prof. L. R. Wilberforce \*, and a simplification of that method depending upon flexural vibrations of a straight piece of wire has been given by Mr. G. F. C. Searle †. The apparatus described in the present paper yields an oscillation method which is fairly simple, and it has the additional advantage that without any change of the apparatus a statical measurement of the stretch modulus can also be easily made.

If a horizontal bar AB, fig. 1 (hereafter called the needle), is symmetrically supported by two equal parallel wires *pq*, *rs*, it may be made to execute a small oscillation in the plane of the paper about an axis passing through the middle point of *qs* perpendicular to the plane of the paper. This oscillation is accompanied by alternate extension and contraction of the supporting wires, so that the resistance to stretching of these wires controls the oscillation and determines its period. The period of the oscillation for a given pair of wires may be made of any convenient length by altering the moment of inertia of the needle. Some of the dimensions of the apparatus can be eliminated by observing other modes of oscillation of the system: so that in its simplest form the experiment gives an expression for the stretch modulus involving only four periods and the weight of the needle, quantities which can be measured with ease and accuracy.

In the statical method a small weight is hung on the needle at a measured distance from the centre. This produces

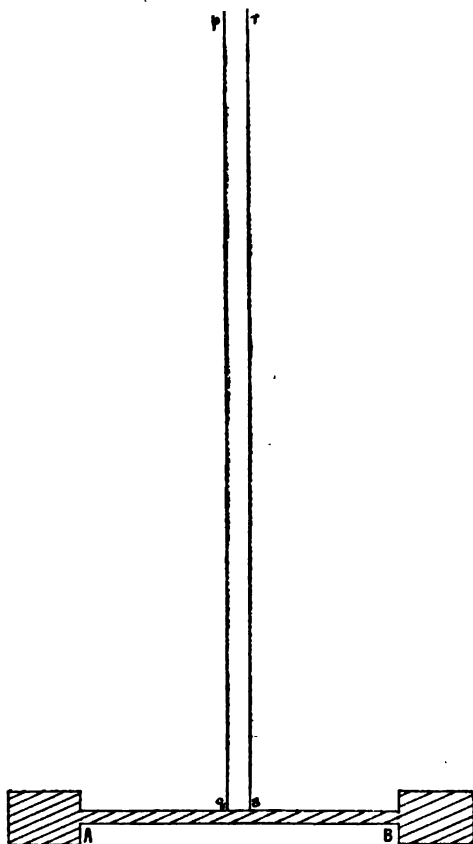
\* Read November 22, 1901.

† Phil. Mag. Oct. 1894.

‡ Ibid. Feb. 1900.

a known difference between the tensions in the wires, and the consequent difference in extension can be measured on a

Fig. 1.



scale by a beam of light reflected from a small mirror attached to the needle. By hanging the small weight at various distances a series of measurements can be made.

#### I. FIRST OSCILLATION METHOD.

*The Needle.*—The vibrating needle AB may be conveniently made of a straight bar or tube with a heavy cylinder fixed at each end of the bar by set screws. If these cylinders are

hollow, and each made with four set screws placed as shown in figs. 2 and 3, their positions can easily be adjusted in

Fig. 2.

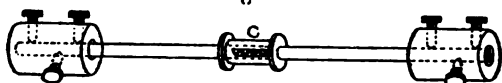
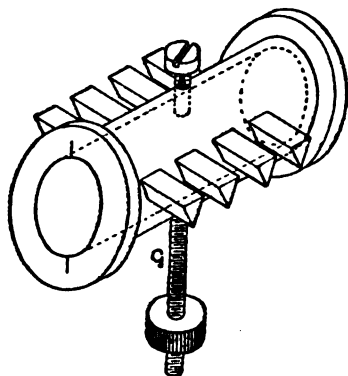


Fig. 3.



any way that may be required. The centre of the bar is fixed with a set screw into a short flanged tube, fig. 4, and

Fig. 4.



C fig. 2, with two pairs of parallel knife-edges projecting from the sides. These knife-edges rest on double hooks,

Fig. 5.

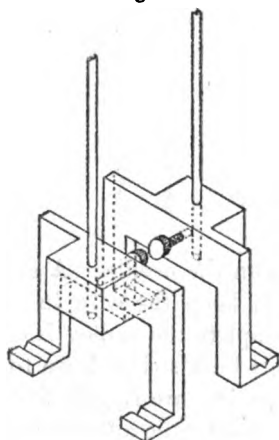
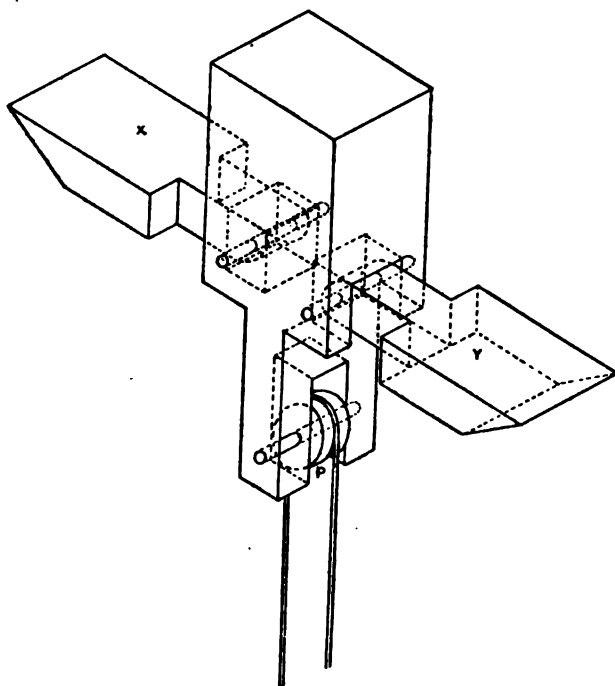


fig. 5, which hang from the suspending wires. This flanged  
Q 2

tube with the knife-edges carries also a vertical screw with a nut—a gravity bob—for adjusting the position of its centre of gravity.

*The Suspension.*—The parallel wires to be stretched consist of a single length of wire with its ends fixed below to the hooks supporting the needle, and passing above over a pulley, P (fig. 6), of diameter equal to the distance between the

Fig. 6.



parallel knife-edges on the needle. A slight groove is made round the pulley to keep the wire in position. After the adjustments are complete the pulley is clamped between the blocks X, Y, fig. 6, which swing down to each side of it, so that the suspending wires are rigidly fixed at the top.

*Adjustment.*—To adjust the apparatus the needle is placed with its knife-edges on the hooks, and while the pulley is



free to turn the needle is adjusted until it rests in a horizontal position. The centre of gravity of the needle is then in a vertical line midway between the suspending wires. The pulley is then clamped, and the equality of tension of the wires tested by seeing that they give the same note when struck. If now the centre of gravity of the needle is at the same level as the knife-edges, the pitching oscillation will be due entirely to the stretching and contraction of the wires. If in practice, however, the centre of gravity does not occupy exactly this position, the effect of a small error in this respect proves to be so small that it may usually be neglected. In any case it can be allowed for. The calculations are given below. The position of the centre of gravity of the central tube can be separately adjusted to the right level by means of the gravity bob, G, fig. 4, which is attached to the tube for that purpose. And as the weight of the central tube is a very small fraction of the whole weight of the needle, any outstanding error in the position of its centre of gravity would be quite inappreciable in its effect.

In the bifilar oscillation the period is affected by the resistance to torsion of the wires. This effect is eliminated by observing the periods with the needle suspended by first the inner, and second the outer pair of knife-edges, so that the suspending wires are at two different distances apart. The supporting pulleys on which the wires are clamped at the top are made of diameters equal to the distances between the knife-edges, so that the wires are parallel in each experiment. The free lengths of the wires are taken the same in each experiment; this can be secured automatically by an appropriate arrangement of the pulleys.

*Calculation of the Periods.*—Of the oscillations possible to this system we shall make use of three. They are rotations about three perpendicular axes through the centre of the needle, viz. :—

1. About a vertical axis—the bifilar oscillation.
2. About a horizontal axis perpendicular to the length of the needle—pitching.
3. About a horizontal axis along the length of the needle—rolling.

Let  $l$  be the length of each of the wires,  
 $M$  the mass of the needle,  
 $\lambda$  the modulus of stretching of each of the wires,  
 $\tau$  the modulus of torsion of each of the wires,  
 $k_2$  the radius of gyration of the needle about its axis of figure,  
 $k_1$  the radius of gyration of the needle about an axis perpendicular to its axis of figure through the centre of gravity. The needle is made a figure of revolution so that this radius of gyration may be taken the same in all such directions.

Firstly, assume that the mass of the hooks on which the knife-edges rest may be neglected in comparison with that of the needle, and that the centre of gravity of the needle is at the same level as the knife-edges. Then the equation of motion of the bifilar oscillation when the wires are distant  $2c$  apart is

$$Mk_1^2\ddot{\theta} = -\left(Mg\frac{c^2}{l} + 2\tau\right)\theta,$$

and the frequency  $n_1$  is given by

$$4\pi^2 k_1^2 n_1^2 = \frac{gc^2}{l} + \frac{2\tau}{M}.$$

Similarly the frequency  $n_1'$  when the wires are distant  $2d$  apart is given by

$$4\pi^2 k_1^2 n_1'^2 = \frac{gd^2}{l} + \frac{2\tau}{M},$$

therefore

$$4\pi^2 k_1^2 (n_1^2 - n_1'^2) = \frac{g}{l} (c^2 - d^2). \quad . \quad . \quad (1)$$

Again, the equation of motion for the pitching oscillation when the wires are distant  $2c$  apart is

$$Mk_2^2\ddot{\theta} = -\frac{2\lambda c^2}{l}\theta,$$

and the frequency  $n_2$  is given by

$$4\pi^2 k_2^2 n_2^2 = \frac{2\lambda c^2}{Ml}.$$

Likewise the frequency of pitching  $n_2'$  when the wires are

distant  $2d$  apart is given by

$$4\pi^2 k_1^2 n_2'^2 = \frac{2\lambda d^2}{Ml}.$$

Therefore

$$4\pi^2 k_1^2 (n_2^2 - n_2'^2) = \frac{2\lambda}{Ml} (c^2 - d^2). \quad . \quad . \quad . \quad (2)$$

Consequently

$$\lambda = \frac{1}{2} M g \frac{n_2^2 - n_2'^2}{n_1^2 - n_1'^2}, \quad . \quad . \quad . \quad . \quad (3)$$

a result requiring no measurement except the periods and the weight of the needle.

Secondly, if the centre of gravity of the needle is at a distance  $x$  below the level of the knife-edges the equation of motion for pitching with the wires  $2c$  apart is

$$M(k_1^2 + x^2)\ddot{\theta} = -\left(\frac{2\lambda c^2}{l} + Mgx\right)\theta,$$

and the frequency is given by

$$4\pi^2 n_2^2 = \frac{2\lambda c^2}{(k_1^2 + x^2)Ml} + \frac{gx}{k_1^2 + x^2}.$$

Likewise the frequency with the wires  $2d$  apart is given by

$$4\pi^2 n_2'^2 = \frac{2\lambda d^2}{(k_1^2 + x^2)Ml} + \frac{gx}{k_1^2 + x^2}.$$

Therefore

$$4\pi^2 (n_2^2 - n_2'^2) = \frac{2\lambda (c^2 - d^2)}{(k_1^2 + x^2)Ml}. \quad . \quad . \quad . \quad (4)$$

The periods of the bifilar oscillation are the same as in the first case. So that equations (1) and (4) give

$$\lambda = \frac{1}{2} M g \frac{n_2^2 - n_2'^2}{n_1^2 - n_1'^2} \left(1 + \frac{x^2}{k_1^2}\right), \quad . \quad . \quad . \quad . \quad (5)$$

as  $x$  is always small compared to  $k_1$ .  $x^2/k_1^2$  is usually negligible, and when this is so equation (5) reduces to (3).

Thirdly, to allow for the hooks supporting the knife-edges, let  $m$  be the sum of their masses, and  $k_3$  their radius of gyration about a vertical axis through their common centre of gravity. Then if  $n_4$  and  $n_4'$  are the frequencies of pitching, and  $n_3$  and  $n_3'$  of bifilar oscillation with the wires distant  $2c$

and  $2d$  apart respectively, we have

$$4\pi^2 n_3^2 = \frac{gc^2}{l} \cdot \frac{M+m}{Mk_1^2 + mk_3^2} + \frac{2\tau}{Mk_1^2 + mk_3^2},$$

$$4\pi^2 n_4^2 = \frac{2\lambda c^2}{l} \cdot \frac{1}{Mk_1^2 + mc^2},$$

and corresponding equations with  $d$  substituted for  $c$ .

Thus we get . . .

$$\lambda = \frac{1}{2}(M+m)g \frac{n_3^2 - n_4^2}{n_4^2 - n_1^2} \left( 1 + \frac{m}{M} \cdot \frac{c^2 + d^2 - k_3^2}{k_1^2} \right), \quad (6)$$

since  $m$  is small compared with  $M$ , and  $c$ ,  $d$ , and  $k_3$  are small compared with  $k_1$ . When the fraction in the last bracket is negligible, or when the hooks are so shaped that  $k_3 = \sqrt{c^2 + d^2}$ , equation (6) reduces to the original result of (3).

## II. SECOND OSCILLATION METHOD.

In certain cases it is necessary to clamp the wires direct to the needle instead of attaching them to hooks which support the needle by knife-edges. In this case flexure of the wires has to be taken account of.

In the bifilar oscillation the effect of flexure is negligible.

In the rolling oscillation when the centre of gravity is at the same level as the points of attachment of the wires there is a quick oscillation due entirely to the resistance to flexure of the wires.

In the pitching oscillation both stretching and flexure of the wires are involved. The influence of flexure alone may be ascertained from the rolling oscillation, and by allowing for this in the pitching oscillation the stretch modulus may be deduced.

This method has the disadvantage of requiring the moments of inertia of the needle to be separately determined. This, however, can be avoided by the following modification of the experiment.

If the centre of gravity of the needle is raised above the level of the points of attachment of the wires the period of the rolling oscillation is lengthened; and by suitably adjusting the height of the centre of gravity this period may be made

infinite. In that case the effect of gravity exactly counteracts the effect of flexure for a small rolling displacement. This being so, if we set the needle to pitch, the effects of gravity and of the flexure will still exactly counteract each other, and the resistance to stretching of the wires will alone control and determine the period of the pitching.

In adjusting the apparatus for this experiment it is necessary to take care that the moments of inertia involved in the bifilar and pitching oscillations are equal. This may be secured by fixing at each end of the bar of the needle a cross consisting of four equal screws at right angles to the length of the needle, two horizontal and two vertical. Nuts on these screws afford a convenient means of adjusting the position of the centre of gravity and the moments of inertia.

For the determination of the stretch modulus, however, this adjustment of the centre of gravity is not necessary. The double observation which eliminates the effect of torsion eliminates at the same time the effect of flexure of the wires.

The equation of motion of the pitching oscillation may be written

$$Mk_1^2\ddot{\theta} = -\left(\frac{2\lambda c^2}{l} + f\right)\theta,$$

where  $f\theta$  expresses the couple due to flexure, this couple being independent of the distance between the wires. The frequencies of pitching with the wires  $2c$  and  $2d$  apart respectively are given by

$$4\pi k_1^2 n_2^2 = \frac{2\lambda c^2}{Ml} + \frac{f}{M}$$

and

$$4\pi k_1^2 n_1^2 = \frac{2\lambda d^2}{Ml} + \frac{f}{M},$$

so that

$$4\pi k_1^2 (n_2^2 - n_1^2) = \frac{2\lambda}{Ml} (c^2 - d^2). \quad . \quad . \quad (7)$$

The bifilar periods still satisfy equation (1), so that

$$\lambda = \frac{1}{2} Mg \frac{n_2^2 - n_1^2}{n_1^2 - n_2^2},$$

as before.

## III. STATICAL METHOD.

The apparatus of the first method also lends itself readily to the statical measurement of the stretch modulus. Let the bar of the needle be divided in centimetres and let a small weight, say 100 grams, be hung on the needle at a succession of measured distances from the centre. Then in each position the small weight produces a known difference in the tensions of the suspending wires, and with a small mirror attached to the needle, the differences of extension of the wires may be read by a beam of light reflected on to a scale.

If the small mass hung on the needle is  $w$ , the distance between the vertical wires is  $2a$ , and the distance of the scale from the mirror on the needle is  $h$ , it is easily seen that if a displacement  $z$  of  $w$  along the needle produces a displacement  $y$  of the spot on the scale,

$$\lambda = \frac{1}{2}wg \cdot \frac{lh}{a^2} \cdot \frac{z}{y}. \quad . \quad . \quad . \quad . \quad (8)$$

For if the displacement  $z$  of  $w$  turns the needle through an angle  $\theta$ , one wire is stretched  $2a\theta$  more than the other, and the tension on that wire is increased by an amount  $\frac{wgz}{2a}$  more than the tension on the other. So that

$$\frac{wgz}{2a} = \lambda \cdot \frac{2a\theta}{l} = \lambda \cdot \frac{2a}{l} \cdot \frac{y}{2h}.$$

The chief precaution required in this experiment besides those usual in measuring a stretch modulus is to place the mirror so that the displacement of the spot on the scale due to the bifilar motion of the needle is at right angles to that due to the stretching of the wires.

XVII. *Contributions to the Theory of the Resolving Power of Objectives.* By Professor J. D. EVERETT, F.R.S.\*

IN high class objectives, both of telescopes and microscopes, the practical limit to the power of separating close points (called *resolving power* or *separating power*) depends upon the blurring due to diffraction. Owing to diffraction, the image formed of a bright point is not a point, but a spot, brightest in the central part, and falling off without any discontinuity from the centre to the margin. In favourable circumstances this spot is surrounded by a succession of bright rings. The phenomenon is seen in its greatest perfection when small aperture is combined with good definition. Blocking out the central portion of the objective makes the spot smaller and the surrounding rings relatively brighter.

Dawes (Mem. R. Astr. Soc. xxxv. p. 158) made very elaborate observations on double stars for the purpose of investigating the separating power of telescopes; and arrived at the conclusion that the angular distance between the two components, when they are nearly equal in magnitude, and are just separated, is given by the formula—

*4.56 seconds, divided by diameter of objective in inches.*

The first calculation of the relative brightness at different points of the spot and rings, which constitute the diffraction image of a point formed by a lens symmetrical round an axis, was published by Airy in 1836 (Camb. Trans. v. p. 283), in a very clear and readable paper. His basis of procedure is the very direct and intelligible one of considering the concave wave-front which advances from the objective to the focus, and computing, for its initial position, the “disturbance” which it produces (according to Huygens’ principle) at any given small distance measured laterally from the geometrical focus.

Another principle of calculation, less obviously correct but leading to precisely the same result, is employed in Mascart’s *Optique* and in Preston’s ‘Light.’

Both methods of procedure lead to one and the same infinite series for the “disturbance” at given lateral distance

\* Read February 28, 1902.

from the geometrical focus ; and this series is a Bessel's function of the first order. It is in fact  $\frac{2J_1(m)}{m}$ ,  $m$  denoting  $\frac{2\pi R}{\lambda f} b$ , where  $R$  is radius of aperture,  $f$  focal length,  $b$  lateral distance, and  $\lambda$  wave-length. The calculation assumes identity of disturbance both in degree and in kind at all points of the wave-front.

A simple calculation (given at p. 277 of my *Deschanel*, Part iv.) shows that the extreme difference of optical path, for disturbances coming from different points of a concave wave-front to a point at lateral distance  $b$  from the geometrical focus (the centre of the sphere to which the wave-front belongs), is  $2b \sin \alpha$ ,  $\alpha$  denoting the angular radius of the wave-front as seen from the focus. When the extreme difference of path is  $\lambda$ , we have therefore

$$b = \frac{\lambda}{2 \sin \alpha} . . . . . (1)$$

Comparison with observation shows that this value of  $b$  represents with fair accuracy the limit of separation. The angle subtended by the distance  $b$  at the second nodal point of the objective, which is identical with the angle subtended by the corresponding distance in the object, as seen from the first nodal point, is

$$\frac{b}{f} = \frac{\lambda}{2f \sin \alpha} = \frac{\lambda}{D}, . . . . . (2)$$

$f$  being the focal length, and  $D$  the diameter of the objective. This formula  $\lambda/D$  for the least distance between the components of a double star, agrees with Dawes's value above quoted, if we put  $\lambda = .000022$  inch = .56 micron. The wave-length for the brightest rays is usually taken as .55 micron, which is as good an agreement as could be desired.

Passing now to the case of the microscope, and supposing the same formula for the minimum distance  $b$  in the image to be still applicable, we may conveniently transform it by means of the equation (which we shall discuss later)

$$\mu_1 y_1 \sin \theta_1 = \mu_2 y_2 \sin \theta_2 . . . . . (3)$$

applicable to any optical system which gives sharp flat images.



In this equation,

$y_1$   $y_2$  denote the distances of a point of the object, and the corresponding point of the image, from the axis of the system ;

$\mu_1$   $\mu_2$  the indices of the first and last media ;

$\theta_1$   $\theta_2$  the angles made with the axis by any incident ray and the corresponding emergent ray.

The ratio  $(\mu_1 \sin \theta_1)/(\mu_2 \sin \theta_2)$  is equal to the magnification  $y_2/y_1$ , and is therefore the same for all values of  $\theta$ . This constancy is called by Abbe the *sine condition*.

In the present case  $\theta_2$  is  $\alpha$ ,  $y_2$  is  $b$ ,  $\mu_2$  is 1 ; and if  $\alpha_1$  denote the obliquity of an extreme incident ray, the equation gives

$$\mu_1 y_1 \sin \alpha_1 = b \sin \alpha ,$$

$$y_1 = \frac{\sin \alpha}{\mu_1 \sin \alpha_1} b = \frac{\sin \alpha}{\mu_1 \sin \alpha_1} \cdot \frac{\lambda}{2 \sin \alpha} = \frac{\lambda}{2 \mu_1 \sin \alpha_1} = \frac{\lambda_1}{2 \sin \alpha_1} . \quad (4)$$

$\lambda_1$  denoting the wave-length in the first medium which corresponds to  $\lambda$  in air. This value for  $y_1$ , the distance between points or lines which can be barely separated, has been extensively adopted. Helmholtz in the *Jubelband* of Pogg. *Ann.* 1874, p. 557 adopts it in the form last written. Abbe calls  $\mu_1 \sin \alpha_1$  the *numerical aperture* of the objective, and adopts the formula *wave-length divided by twice the numerical aperture*. Drude (*Lehrbuch der Optik*) adopts it as the limiting distance for oblique illumination, and its double as the limiting distance for direct illumination.

Microscopic test-objects are not self-luminous like double stars, but are viewed by transmitted light. If no condensing arrangement is employed, the pencil of light sent by a point of the object to the objective consists of rays from different parts of the source, that is, in effect, from different sources. An orthogonal section of such a pencil does not possess the characteristic properties of a wave-front. Different portions of it have no definite relation of phase, and are incapable of mutual interference. Our formulæ are therefore no longer applicable. Practically we may regard such an orthogonal section as made up of a number of small parts, each of which is a wave-front, giving by reason of its smallness a very large diffraction image of a point of the object. These

separate images of the same point overlap without interference, and as they do not exactly coincide, compose a larger and more blurred image of the point represented.

The cure for this evil is furnished by employing a condenser of high quality, to throw upon the part of the object under examination a very sharp image of the source of illumination. If the image were perfectly sharp, each point of the object would get its light from its own special point of the source, and the effect would be to make the object act as if it were self-luminous. Each point of the object would send to the objective a pencil whose orthogonal sections would be true wave-fronts, to which our previous reasoning would be applicable ; so that the diffraction spot which represents a point would have the small size due to the largeness of the entire aperture.

This appears to me to be the chief benefit conferred by sharply focussing the source on the object ; but it has not so far as I am aware been pointed out by any writer on the microscope hitherto. Abbe in his great paper on microscopic perception (*Archiv für mikr. Anat.* ix. p. 413, 1873) regards the condenser merely from the point of view of geometrical optics, and recommends the use of one which is not achromatic. Microscopic observers long ago ascertained, as an empirical fact, that achromatic condensers gave better results than non-achromatic ; while mathematicians refused to believe them, and maintained that achromatism could be of no advantage, seeing that the sole purpose of a condenser was to give wide pencils of strong light.

There is another advantage from sharp focussing by the condenser, which may be regarded as the complement of that above indicated. If the focussing were perfectly sharp, the waves from one point of the object could not interfere with waves from another point. Such interference gives rise to spurious diffraction patterns, liable to be mistaken for structures existing in the object. The two components of a double star exhibit no mutual interference in a telescope ; and different points of a microscopic object cannot produce mutual interference if they send light which has come from completely distinct sources. Lord Rayleigh (*Phil. Mag.* xlii. 1896) was, I believe, the first to indicate this advantage. Abbe, in his

paper on microscopic perception, makes no allusion either to the focussing of the source on the object, or to the finite size of the spot which (with its surrounding rings) is the diffraction image of a single isolated point.

The following explanation of the advantage of oblique illumination is, I believe, new.

Perfect sharpness of focussing by a condenser is unattainable; and two points of the object which are not further apart than twice the limiting distance of separability will inevitably have a portion of the source in common, as regards their illumination. Let  $\beta$  denote the obliquity of the illumination, the two object-points in question being supposed to be in a plane which contains the illuminating rays and the axis of the objective. The difference of optical path for rays coming from the same point of the source to the two object-points is  $s \sin \beta$ ,  $s$  denoting the distance between the two points. The best condition for separation is, that this difference of path shall be half a wave-length in the medium in which the object is immersed (say  $\frac{1}{2}\lambda_1$ ), for this gives the most complete extinction in the overlapping portion of the two diffraction spots which are the images of the two points. Putting then

$$s \sin \beta = \frac{1}{2}\lambda_1, \quad . . . . . (5)$$

and assigning to  $s$  the value  $\lambda_1/\sin \alpha_1$ , which being double of the accepted minimum value may be taken as representing an ordinary test, we deduce

$$\sin \beta = \frac{1}{2} \sin \alpha_1 . . . . . (6)$$

If we put  $s$  equal to the accepted minimum itself, we obtain

$$\sin \beta = \sin \alpha_1 . . . . . (7)$$

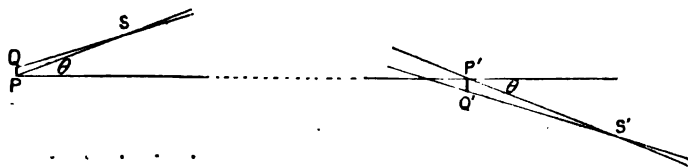
These conclusions agree with the received view among microscopists, that the obliquity of illumination should be rather less than the obliquity of the extreme rays of the incident pencil.

*Note on Hockin's proof of the Sine Condition.*

Various proofs have been given of the sine condition expressed by equation (3), which must be fulfilled in every case in which a sharp image, in a plane perpendicular to the

axis of the instrument, is formed of a small flat object whose plane is perpendicular to the axis. By far the simplest is that given in an article "On the Estimation of Aperture in the Microscope," published after the author's death in the Journal of the Royal Microscopical Society (1881, ser. 2, iv. p. 337), where he is described as the late Mr. Charles Hockin, junr., an electrician and mathematician of repute. Appreciative notes by Abbe are inserted in the article. Strange to say, the proof does not seem to have been reproduced in any English publication, though it is to be found, modified for the worse, in German optical treatises. In Müller-Pouillet it is erroneously described, and the author's name is given as John Hockin. These circumstances, in conjunction with the great importance of the theorem itself, are my reasons for reproducing it. I have corrected a clerical error of — for + in the two principal equations.

Let  $PP'$  in the figure represent the axis of an optical



system which gives the linear image  $P'Q'$  of the small object-line  $PQ$ , both the lines  $PQ$  and  $P'Q'$  being perpendicular to the axis. The incident pencils may be of large angle; and the image is supposed to be *aplanatic*, that is to say, all rays sent by  $P$  pass through  $P'$ , and all rays sent from  $Q$  pass through  $Q'$ . Let  $PS$  be any one of the rays sent from  $P$ , and  $QS'$  a ray from  $Q$  intersecting it at  $S$ .

Since  $PQ$  is small, the angle  $PSQ$  is small, and the plane pencil bounded by  $PS$ ,  $QS$  will give an emergent pencil bounded by  $P'S'$ ,  $Q'S'$ , the optical path from  $S$  to  $S'$  having the same value for all the rays of the pencil; denote this value by  $(SS')$ .

Then, if  $\mu$  be the index of the first and  $\mu'$  that of the last medium, the optical path from  $P$  to  $P'$  is

$$\mu \cdot PS + (SS') - \mu' \cdot P'S',$$

and is constant for all rays that go from P to P'. Similarly the optical path from Q to Q' is

$$\mu \cdot QS + (SS') - \mu' \cdot Q'S',$$

and is constant. Subtracting, and denoting the difference of the two constants by  $c$ , we have

$$\mu(PS - QS) - \mu'(P'S' - Q'S') = c,$$

or (calling the obliquities  $\theta, \theta'$ ),

$$\mu \cdot PQ \sin \theta - \mu' P'Q' \sin \theta' = c.$$

But  $\theta$  and  $\theta'$  vanish together, therefore  $c$  is zero; and we have

$$\mu \cdot PQ \sin \theta = \mu' \cdot P'Q' \sin \theta'. \quad . \quad . \quad . \quad (3)$$

The ratio of  $\mu \sin \theta$  to  $\mu' \sin \theta'$  has therefore the constant value  $P'Q'/PQ$  for all the rays by which the image is formed.

The present paper has been framed with a view to supplementing two papers by Lord Rayleigh, one of them (in two parts) in the *Phil. Mag.* for the second half of 1879, and the other (which has been already quoted) in *Phil. Mag.* vol. xlii. 1896. They contain a much fuller treatment of the theory of resolution than I have met with elsewhere.

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### XVIII. *Note on the Compound Pendulum.*

By S. A. F. WHITE, M.A.\*

[Abstract.]

IN the determination of the length of the simple equivalent pendulum for a compound pendulum, whose form is a symmetrical bar and bob with one fixed, one movable knife-edge and no sliding weight, it is convenient to make the mass of the movable knife-edge small. In this case small displacements of this knife-edge will not materially alter the position of the centre of gravity or the radius of gyration of the whole pendulum about an axis through its centre of

\* Read April 25, 1902.

gravity, and the time of oscillation about the fixed knife-edge will remain practically constant.

The best determination of the correct position of the movable knife-edge for an equal time of oscillation will be given when, for a given displacement of this knife-edge, there is the greatest variation in the time of oscillation about it. If  $k$  = the radius of gyration of the pendulum about an axis through its c. g. parallel to the axis of suspension,  $h$  = the distance of the axis of suspension from the c. g.,  $t$  = the time of one complete oscillation,

$$t = 2\pi \sqrt{\frac{h^2 + k^2}{hg}}$$

$$\therefore \frac{\sqrt{g} dt}{2\pi dh} = \frac{1}{2} \sqrt{\frac{h}{h^2 + k^2}} \frac{h^2 - k^2}{h^2}$$

Critical values of  $\frac{dt}{dh}$  occur when

$$\frac{d}{dh} \sqrt{\frac{h}{h^2 + k^2}} \frac{h^2 - k^2}{h^2} = 0.$$

From this we see a maximum value of  $\frac{dt}{dh}$  occurs when  $h = 2.54 k$ .

Assume a pendulum having the form of a brass bar, length  $x$ , breadth  $a$ , and thickness  $t$ , fitting into a lead block, length  $y$ , breadth  $b$ , and thickness  $T$ , and let the ratio of the dimensions be

$$\frac{x}{y} = 10, \quad \frac{a}{b} = \frac{1}{2}, \quad \frac{t}{T} = \frac{1}{2},$$

then the mass of the lead block will be very approximately twice that of the bar.

If we make  $a = \frac{1}{4}x$  we find  $x = 3.23 k$ . Making  $x = 100$  cms.,  $k = 30.96$  cms., and the distance of the c. g. from the top of the bar = 86.6 cms.

Also  $2.54 k = 78.64$  cms., so that if the movable knife-edge is 8 cms. from the top of the bar we have  $h = 2.54 k$  and a maximum value of  $\frac{dt}{dh}$ .

The corresponding length of the simple equivalent pendulum is 90.7 cms., so that the fixed knife-edge comes conveniently near the bottom of the brass bar and not in the lead block.

[For a seconds pendulum the value of  $\alpha$  should be 110 cms.]

The calculated value of  $\frac{dt}{h} = \cdot 009$  sec. per cm. So that for 1 cm. change of position of the movable knife-edge there is nearly 1 sec. change in the time of 100 complete oscillations.

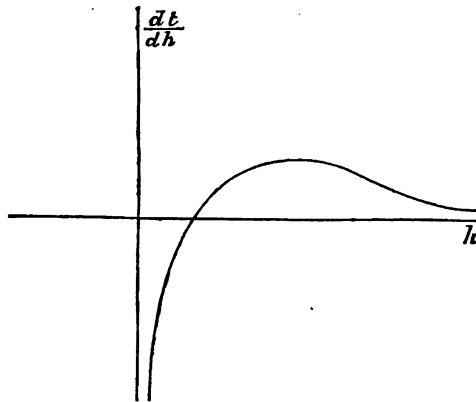
In an experimental pendulum constructed on the above lines, the upper knife-edge was movable in a slot cut in the brass bar, the mass of the knife-edge approximately compensating the mass of the brass removed for the slot. The length of the brass bar was 98·8 cms., and the length of the slot 2·83 cms.

Time about movable knife-edge when at	top of slot	= 1·921 secs.
“ “ “ “ “	bottom of slot	= 1·894 secs.

Giving  $\frac{dt}{dh} = \cdot 0095$  sec. per cm., which agrees well with the calculated value.

The length of the simple equivalent pendulum was found to be 91·4 cms. when  $t = 1\cdot 918$  secs., giving the value of  $g = 981\cdot 4$ .

The ratio of  $h$  to  $k$  was 2·59, which differs little from the calculated ratio for a maximum value of  $\frac{dt}{dh}$ .



The curve showing the variation of  $\frac{dt}{dh}$  with  $h$  has the form

R 2

given in the figure. When  $h < k$ ,  $\frac{dt}{dh}$  increases rapidly but is negative. When  $h = 2.54 k$ ,  $\frac{dt}{dh}$  is a positive maximum, and any error in the observed time of oscillation about the fixed knife-edge should produce an error of the same sign in the length of the simple equivalent pendulum.

#### DISCUSSION.

Dr. CHREE said that the mathematical work might apply to either of two distinct problems. It might refer to the case of an ordinary pendulum with one movable knife-edge, the object sought being the particular position in which a given change in the period answered to the greatest movement of the knife-edge. The second case, the one which he supposed the author had in view, was that of a Kater pendulum, the object being to ascertain what design enabled the position of the movable knife-edge to be most accurately determined from the condition that the period about it should equal that about the fixed knife-edge. The author's reasons for neglecting the solutions answering to a short pendulum of large moment of inertia did not appear mathematically complete, though they might be supported from physical considerations as to the relative accuracy of the determinations of " $g$ " with long and with short pendulums.

Mr. WATSON said that, so far as the accuracy of the result was concerned, the distance between the knife-edges was the determining factor. The position of the movable knife-edge for strict equality of period could be deduced by interpolation from periods determined in two positions of the movable edge. In accurate work, a light bob equal in size to the heavy bob might be placed upon the other end of the pendulum to keep the air friction constant.

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XIX. *Note on a Temperature Indicator for use with Platinum Thermometers in which the Readings are Automatically Reduced to the Gas Scale.* By ROBERT S. WHIPPLE\*.

IN 1887 Prof. Callendar pointed out † that if  $R_0$  denotes the resistance of the spiral of a particular platinum thermometer at  $0^\circ$ , and  $R_1$  its resistance at  $100^\circ$ , a temperature-scale may be established for the particular wire, this scale being called the *scale of platinum temperatures*, such that if  $R$  be the resistance at any temperature  $T^\circ$  on the air-scale, this temperature on the platinum scale will be  $\frac{R-R_0}{R_1-R_0} \times 100^\circ$ . For this quantity he employed the symbol *pt*, its value depending on the sample of platinum chosen.

In order to reduce to the standard scale of temperature the indications of any platinum thermometer, it is necessary to know the law connecting  $T$  and *pt*. These are of course identical at  $0^\circ$  and  $100^\circ$ ; but the determination of the remainder of the curve expressing the relationship between them is a matter of experiment.

The work of Prof. Callendar established for pure platinum the relation

$$d = T - pt = \delta \left[ \left( \frac{T}{100} \right)^2 - \frac{T}{100} \right].$$

The value of  $\delta$  depending on the purity of the platinum employed.

When working with platinum thermometers it is usual to calculate a table of corrections for converting the temperatures on the platinum scale to the corresponding temperatures on the gas- or air-scale for the particular sample of platinum wire used. Some of these tables have been published, notably those by Drs. Harker and Chappuis ‡ for several values of  $\delta$ . These tables are of the greatest assistance to the worker in platinum thermometry.

The instrument which I am bringing to your notice is very similar to the well-known Callendar & Griffiths' Temperature

\* Read April 25, 1902.

† Callendar, Phil. Trans. vol. clxxxii. p. 147.

‡ Harker and Chappuis, Phil. Trans. vol. cxciv. pp. 118-128.

Indicator, with the exception that it is so arranged that the readings obtained are automatically reduced to the gas-scale, thus avoiding the necessity for the correction referred to above.

It consists of a simple Wheatstone-bridge with equal ratio coils, the other arms being the thermometer and a long helical bridge-wire, together with the compensating leads of the thermometer. A travelling contact is moved round the wire until a balance is obtained. The balance point is indicated by means of an index attached to the coil of a D'Arsonval galvanometer.

The bridge-wire is wound in a helix cut on the outside of an ebonite drum, the contact being mounted on the inner surface of a drum which can be moved over the bridge-wire by means of a screw of the same pitch as the helix.

The scale is divided on the outer face of this drum and passes under a reading-index fixed above it. The scale has been calculated so that the values obtained with a platinum thermometer having a " $\delta$ " of 1.5 are given on the gas-scale. The scale is an open one, the length of a degree-division ranging from 5 mm. at  $10^{\circ}$  to 3 mm. at  $1350^{\circ}$  C.

As there are no coils in series with the bridge-wire, rapidly varying temperatures can be easily followed.

The instrument is self-contained, galvanometer, battery, etc., packing into a case  $27 \times 20 \times 22$  centims. It was constructed by the Cambridge Scientific Instrument Co.

[*Note added Oct. 1902.*—I was not aware when designing the above instrument that Mr. Rollo Appleyard had suggested the idea of calibrating directly a bridge-wire in temperature degrees. See "A Direct Reading Platinum Thermometer," *Phil. Mag.* Jan. 1896.

#### DISCUSSION.

Dr. CHREE asked the following questions :—Was not the instrument as constructed restricted to platinum thermometers of wire having a given specified value of  $\delta$  ; if so, what was this value ? Did the helical wire balance the entire resistance of the thermometer, or only the excess above the resistance at  $0^{\circ}$  C., and could the instrument measure temperatures below  $0^{\circ}$  C. ? What error was likely to come in when measuring temperatures up to  $1000^{\circ}$  C. from changes in the resistance of the helical wire under the variations of

atmospheric temperature to which it would be exposed in ordinary use? Would there not be some wear between the wire and the contact-piece?

Dr. HARKER asked what were the limits of the value of  $\delta$  for wires now supplied for commercial purposes. He thought that the accumulation of dust between the contact-piece and the wire, due to continual scraping, was a more serious objection than the wearing away of the wire.

Mr. WHIPPLE said that the value of " $\delta$ " for recent samples of wire seldom exceeded 1.52, and that the " $\delta$ " of the wire generally employed in thermometers, even for commercial purposes, was 1.50. The bridge-wire in the instrument shown balanced the rise of temperature above  $0^{\circ}\text{C}$ ., but there would be no difficulty in adjusting the instrument to read below zero. The maximum error that could possibly arise owing to variations in the temperature of the instrument would not exceed  $0.1^{\circ}\text{C}$ . In reply to Dr. Harker, the contact on the bridge-wire being a potential one, any increase in its resistance did not affect the reading. The wear between the contact-piece and bridge-wire was very slight.

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XX. *Account of the Exhibitions at the Meeting held  
on Friday, April 11, 1902.*

Dr. R. A. LEHFELDT exhibited an "Electric Heater." The apparatus consisted of a vacuum-jacketed glass tube containing water which was boiled by passing a current through a platinum spiral immersed in the liquid. Tap water is preferable to distilled water because the small electrolytic action in the former case causes the boiling to proceed quietly. Different temperatures can be obtained by using other liquids.

Mr. WATSON gave a list of liquids which he had found suitable for boiling electrically. He had used this method of obtaining a steady temperature in an apparatus for comparing thermometers.

Mr. P. H. GRANT exhibited and described "An Apparatus for Vapour-pressure Measurements." The liquid of which

the vapour-pressure is required is introduced into the vacuum of a syphon barometer. This is mounted alongside an ordinary syphon barometer, and the upper extremities of both are surrounded by a bath which can be kept at any desired temperature. The levels of the mercury in the open tubes are then adjusted until the upper mercury surfaces are at the same level. The vapour-pressure is then measured by the difference of level in the open tubes. By a simple modification it is easy to investigate the vapour-pressure of a liquid in the presence of air. The two chief advantages of the method are (1) the avoidance of the temperature correction, and (2) the wide range of temperature over which it can be employed with the use of a small bath.

Prof. CALLENDAR referred to the advantages of the apparatus, and said that it appeared specially suitable for elementary laboratory measurements.

Mr. J. T. MORRIS showed an experiment illustrating the use of Cathode Rays in Alternate Current work. The usual form of Braun tube was used, the rays falling upon a luminescent screen and forming a blue spot. A solenoid conveying an alternating current was fixed near the tube, and the varying magnetic field caused the spot to oscillate about its mean position. To determine the maximum value of the current, a switch should be arranged to rapidly replace the alternating current by a continuous one. The continuous current is then adjusted until the maximum excursion of the spot is the same as before, and the value of the current read off from an ammeter in the circuit. For accurate work, the frequency of the discharge from the induction-coil exciting the tube should be adjusted until it is almost exactly in synchronism with the alternating current. The unsteadiness of the spot of light in the zero position limits the accuracy of the measurements. Mr. Morris has tried to reduce this unsteadiness by using an earthed aluminium diaphragm instead of a glass one.

Dr. HARKER thought the spot of light shown might have been made brighter by the use of a larger coil, and said that the vacuum required careful attention in order to get the best results.

Mr. DUDELL pointed out that the movement of the spot about its zero position might be due to the action of the earth's constant magnetic field upon the varying current passing through the tube.

Mr. WILSON NOBLE suggested that the irregularity in the position of the spot might be due to the irregular sparking of the coil and the consequent irregular magnetic field acting upon the rays.

Prof. S. P. THOMPSON said that the movement was probably due to internal electrostatic causes. He suggested the use of yttria as a luminescent material.

Mr. MORRIS, in reply, said that the earth's field was too weak to account for the variable zero position. He had tried shielding the tube with an earthed copper-wire screen without any appreciable gain in steadiness.

Mr. MORRIS then showed an experiment "On the Growth of Electric Currents in an Inductive Circuit." An E.M.F. of 0.8 volt was applied to a coil wound on a ring-shaped laminated iron core. When the current had attained its steady value the E.M.F. was reversed, and the variations of the current strength shown by an ammeter. About 20 seconds were required for the current to attain its maximum value in the opposite direction. A secondary coil was also wound upon the same core, and the effect produced upon the growing current by the closing of this secondary circuit was shown. Mr. Morris has determined curves of growth for different currents, and he showed how similar curves could be used to determine experimentally the hysteresis loss in transformers.

Dr. GLAZEBROOK drew attention to the fact that this method has been applied, with some slight modifications, to the determination of the hysteresis loss in some 3000 H.P. transformers.

Mr. CROFT showed some apparatus and devices useful in teaching. The method of determining graphically the focal length of a lens from the distances of conjugate foci from the centre was illustrated. The graphical solution of a quadratic equation was also shown. An apparatus for producing and demonstrating the properties of three-phase currents was

exhibited and described. Mr. Croft then showed crystals illustrating the five regular solids, and an electric lamp with the filament in one plane useful for optical work. The flatness of a piece of plate glass can be tested with a scribing block. The point is adjusted to touch the glass in one position. By breathing on the glass, and moving the block about, it is easily seen if the point leaves the surface.

Mr. J. M. BARR said that the method could not be applied to steel. To test the flatness of a piece of steel, he had made use of a table with four legs placed upon the surface. One leg of the table was adjustable, and was made part of a circuit containing a microphone. If the ends of the four legs are placed in one plane, it is easy to test flatness by observing when the adjustable leg leaves the surface. The amount of the irregularity of the surface can be measured by having a micrometer attached to the movable leg.

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## XXI. *A Mechanical Break for Induction Coils.*

*By* Dr. DAWSON TURNER\*.

THE use of induction-coils in the production of Röntgen-rays and in wireless telegraphy has made the construction of a suitable break a matter of importance. The ordinary break is unsuitable because of the wearing away at the point of contact, and there are objections to the use of mercurial breaks. The portable mechanical break which was shown at the meeting consisted of two metallic rollers with their axes parallel and kept in contact by a spring. One of the rollers has a cam attached to its spindle, and can be made to rotate by means of a small electric motor. Once in each revolution the cam separates the rollers, thus making the break, and at the same time causing the second roller, which rides like the first one loose upon its axis, to turn about one-eighth of a revolution. As soon as the cam has passed the rollers are brought into contact by the spring, and the next break occurs at a different place. The wearing is thus distributed evenly over a large surface. The break is placed in a box containing

\* Read April 25, 1902.

water, alcohol, or petroleum, and works best with the latter. An objection to the arrangement is the noise it makes when working. Some experiments were then shown on the discharge of electrified bodies by ultra-violet light. A disadvantage of the electric arc when used to furnish ultra-violet light for use in medicine is that the light is accompanied by heat, so that it is necessary to shield the patient from the heat without interfering with the passage of the light. A condenser spark between iron electrodes is useful because it gives a large amount of ultra-violet radiation without much heat. Dr. Turner showed that this light is capable of discharging bodies whether positively or negatively electrified. He then showed that glass and mica are opaque to the radiation, while pure rock-salt is transparent.

Mr. WILSON NOBLE also exhibited a mechanical break. A roller and a disk, with their axes parallel, are placed in contact and made to rotate in the same direction by a motor. Longitudinal slots are cut upon the surfaces of both, and the break occurs when a slot in the roller comes opposite a slot in the disk. Since the two are moving in opposite directions at their point of contact, the break is very sudden. To vary the length of the break without altering the rate of rotation, the slot in the roller is wider at one end than the other, and the disk can be placed so as to touch the roller at any point of its length.

#### DISCUSSION.

Prof. THOMPSON said he knew of no metal which would withstand continual sparking without wearing, and suggested that breaks should be so designed that the parts affected by the sparking could be easily replaced. He asked if there was any difference in the wear of the two rollers. Referring to an experiment shown by Dr. Turner, in which ultra-violet light discharged a positively electrified body much quicker than a negatively electrified one, he asked if this would be the case if the apparatus were surrounded by an earthed metallic screen.

Mr. WATSON suggested that the wearing of the edges

in Mr. Wilson Noble's break might be lessened by filling the cavities with slate.

Mr. DUDELL said that the worst substance for making contact-pieces was carbon; then came zinc, brass, and copper, with platinum best. These were the results in air, but the effects in liquids were different. With rapidly moving contacts all metals seem equally good, but in ordinary coils the contact-pieces move slowly.

Prof. EVERETT said it was interesting that rock-salt, which is very transparent to long waves, should also be transparent to very short waves.

Dr. DAWSON TURNER said that if the experiment referred to by the Chairman had been performed inside an earthed metallic screen, the negatively electrified body would have been more quickly discharged.

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## XXII. *A Simple Electrical Micrometer.*—Part I.

By P. E. SHAW, B.A., D.Sc.\*

[Abstract.]

Two years ago the Author described an instrument with which he measured very small lengths by the application of electric contacts†, and the micrometer shown was a simple form of the original apparatus. A screw, fitted with a milled head, turns in a fixed nut and its lower end presses upon the extremity of the long arm of a lever. A metal point is attached to the short arm, and the distance through which it moves, on turning the milled head, can be deduced from a knowledge of the pitch of the screw and the ratio between the arms of the lever. In using the instrument either (1) this point, or (2) the screw-point itself (the lever being removed) is brought up to electric contact with the moving body, and the contact is accurately determined by the sounds in a telephone in the circuit. The Author illustrated the use of the instrument for measuring small lengths, by describing

\* Read May 9, 1902.

† Shaw, Phil. Mag. Dec. 1900.



the following eight applications to ordinary laboratory measurements :—

(1) The measurement of the thickness of plates, films, or fibres. The object is placed between two metal plates. The point of the micrometer-screw is adjusted to touch the top plate and the reading taken. The object is removed, the point is again brought into contact with the top plate, and the difference between the readings in the two cases gives the thickness of the film.

(2) The determination of Young's Modulus by the elongation of a wire. The Author described experiments on two wires, each  $2\frac{1}{2}$  metres long, hanging side by side, one of copper and the other of steel. The wires terminated in horizontal platforms to which the stretching weights were attached. The micrometer-screw measures first on to one platform while loads are applied below it, then on to the other platform while loads are applied as before. The first measurement gives the elongation, and the second shows any error due to yielding of the brackets supporting the wires. By reversing the process of measurement we obtain values for the other metal.

(3) The determination of Young's Modulus by the bending of a beam.

(4) The determination of simple rigidity by a static method. Observations were made upon a rod held horizontally by rigid wall brackets. One end of the rod was fixed and the other held in position by a pin pressed into a hole in the end of the rod. From this end an arm projected outwards. Weights were applied to the extremity of this arm, and the twist measured by observing with the micrometer the movement of the end of the arm.

(5) Application as an extensometer.

(6) Measurement of thermal expansion.

(7) Microscopic measurements. In measuring the diameter of a capillary tube the cross wire of a microscope is brought so as to appear to touch one side of the tube, and the point of the micrometer is brought into contact with the metal stage. The stage is then moved by a screw until the cross wire comes to the other side of the tube. The micrometer point is moved into contact again, and the difference

in the readings gives the diameter of the tube. In this measurement the full magnifying power of the microscope is utilized, and the work of moving the stage is performed by a rough screw.

(8) The direct measurement of the wave-length of light. Newton's Rings are formed by a convex lens and a piece of plate glass. The convex lens is fixed to the short arm of the lever, and the distance through which it must be moved to cause a certain number of bands to appear at the centre gives a means of calculating the wave-length of the light employed.

#### DISCUSSION.

Prof. EVERETT said the apparatus combined fineness and accuracy of measurement, and expressed his interest in the determination of distances with the microscope.

Mr. R. J. SOWTER asked if any special precautions had been taken to prevent deformation in the instrument. If not, then it was optimistic to assume that one or more multiplying levers could be used to measure lengths of the order of a millionth of a millimetre with any physical accuracy, assuming the multiplication of measurement to be according to the law of the lever, as Dr. Shaw apparently did.

Mr. W. WATSON said that in determining the wave-length of light by Newton's rings, it was necessary to measure from the knife-edge of the lever to the centre of the rings. The accuracy of the experiment was limited by the difficulty in judging the centre. The variation of the temperature of the air would distort the lever and produce errors. In reference to the experiments on Young's modulus using two wires of different material, he said that no precautions had been taken to procure a steady temperature, and pointed out that variations in temperature would affect the two wires unequally. In the experiment on the torsion of a rod, the twisting had been produced by an unbalanced force. The other arm of the necessary couple must therefore have been unsatisfactorily supplied by the friction of the pin which held the rod in position. In measuring the diameter of a capillary tube with extreme accuracy, it was necessary to have a normal section, which was somewhat difficult to obtain. Dr. Shaw

apparently considered the instrument as suitable for laboratory work. If it was for elementary students it was unnecessarily elaborate, and if for obtaining accurate measurements there were objections and uncertainties which should be investigated. Mr. Watson said that a similar form of micrometer had been described by Mr. H. C. Russell, and used in the observatory at Sydney.

Mr. MARK BARR said that as errors would be introduced by variations in temperature, it might be advisable to make the instrument of a nickel-steel alloy with a small coefficient of expansion. He had known errors to grow even after a steady temperature was reached. He asked if the knife-edges and screws used were good enough to give the same reading twice, and said he thought the limit of physical accuracy could be obtained by using a single disk on a screw calibrated throughout its length. It could almost be stated as a law that for a given ultimate approximate result, error increases more rapidly with the number of links in the mechanism used to attain that result than with the magnitude of the number representing the increased order of fineness required when less links are used. He considered that a screw having a pitch of  $\cdot 25$  mm., which carries a disk divided into 250 parts of  $\cdot 25$  mm. each (giving about an 8 centim. diameter), would give far better results than the complex mechanism shown. Such a screw would give 1 micron advance for each division of the disk; but he believed that one rarely attains an accuracy in construction beyond the limit of one ten-thousandth of an inch. He had exhibited in Paris in 1900 a single screw micrometer used in combination with a telephone receiver.

Dr. SHAW, in reply, said that the main justification of the apparatus was in the consistency of the results given by it; these were excellent, as the tables given in the paper showed. This method had been shown to be much more accurate than most of those in general use. As to the contention that the apparatus, while too sensitive for laboratory practice, was not sufficiently so for research on length changes, he pointed out that the accuracy of all measuring instruments was always on the increase, so that laboratory methods which were considered good recently would not necessarily suffice

in the immediate future. Why be content, even for teaching students, with measuring to the one 50th of a mm. by the microscope, when with the simple electric micrometer we get, with little trouble, to the one 1000th of a mm.? Dr. Shaw knew nothing of the prior publication in Australia mentioned by Mr. Watson; if there were such a method introduced years ago, it was all the more astounding that Mr. Russell and his successors should have allowed such an excellent idea to lapse and remain immature and unknown. Some speakers had suggested that uncertain deformation of the levers might occur during an experiment and vitiate results; but a new strain implied a new stress, and, unless a definite *change* occurred in the forces of the system, we could not suppose a change in deformation. A like answer was given to the criticism that the levers might expand under heat during measurement. Why, if sufficient time had elapsed to allow the system to attain temperature equilibrium, should anyone postulate expansions without indicating a new or irregular source of heat? Most of the above supposed evils of course existed, but they were of small account. As with every good apparatus ever produced, if ordinary and suitable precautions be taken, these errors were reduced to a lower order of importance and could be neglected. In conclusion, the method had been firmly established in University College, Nottingham, and had superseded other apparatus. It would no doubt spread and become general.

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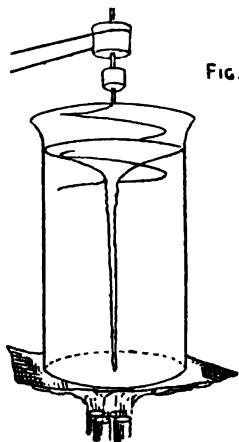
XXIII. *On the Ebullition of Rotating Water.—A Lecture Experiment.* By T. C. PORTER, *Eton, Bucks.\**

If the water in a beaker, having approximately vertical sides, be caused to rotate about an axis concentric with the vertical geometrical axis of the beaker, it is obvious that in any horizontal section of the water the pressure is least in the centre, and increases from the centre outwards. It is also a well-known fact that the temperature at which water boils depends upon the pressure to which it is subjected, being lower the

\* Read May 23, 1902.

lower this pressure is. Thus if a beaker of water were at a temperature just below the boiling-point, and it could be *suddenly* made to rotate throughout its mass without cooling it, the water would turn into vapour in and about the axis of least pressure, from the surface downwards, forming, at all events for the moment, a thin core of steam in the middle of the water. In practice, however, water cannot be made to rotate throughout its mass suddenly; and if the rotation is generated gradually, the water-vapour is also, as a rule, gradually formed, and is given off from the surface without ebullition, in the quantity sufficient to relieve the tension of those particles of water for which the pressure is diminished. The very form taken by the water as it rotates, increases its surface area, and thus tends to promote evaporation, and so to check ebullition. For these reasons the writer has failed to exhibit the experiment to be described in this its simplest form. If, however, the water is supplied with heat whilst it is rotating, the steam is formed only in the region of least pressure, forming a gaseous core in the rotating water, as in fig. 1. The experiment is an exceedingly simple one both to make and to photograph; it may be well to give a few details as to its performance, though the four figures given are only careful drawings from four of the original photographs.

In fig. 1 the spiral wire stirrer used is seen near the surface of the water; whilst beneath the wire gauze, on which the large beaker rests, and which serves to distribute the heat more evenly, are visible the flames and upper parts of the four Bunsen burners employed to heat the water. The spiral stirrer was driven by a small motor; but experience soon proved that results as good, if not better, could be obtained by stirring the water *by hand*, using a long glass rod completely covered by a piece of indiarubber tubing in order to avoid the risk of breaking the glass vessel. After giving to the water



throughout its depth the necessary and rapid rotation, and before taking the photographs, this rod was rapidly withdrawn from the beaker, its stirring motion being carefully maintained during the act of withdrawal. Some of the photographs were taken by diffused daylight combined with that of the electric arc, the latter being concentrated by a lens, so as to illuminate the whole of the beaker and its contents as brightly as possible. The plates were Edwardes's Isochromatic Instantaneous, and the exposures were about the  $\frac{1}{40}$  of a second. A dilute developer should be used, and as much as 30 min. or more allowed for development.

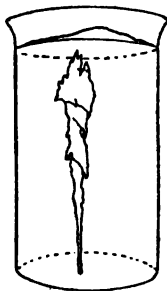
Thus far the experiment illustrates in an apparently simple and beautiful way the lowering of the boiling-point of water under reduced pressure; but there are some very curious phenomena to be presently described, which are shown by the column of steam, if the water is first stirred and then left to come to rest, whilst the heating is continued. Just after the stirrer has been removed, the appearance presented is that recorded in fig. 1.

The lengths of the multitude of curved lines, shown in the original photographs near the bottom of the beaker, and formed by the rotation of small stray bubbles, are an index to the speed with which the water is rotating when the duration of the exposure for the photograph is remembered; and in fig. 1 the rate of rotation is much higher than in the subsequent figures, which are taken at later stages. In fig. 1 there is a markedly concave surface to the water in the beaker, and the column of steam is practically continuous from base to summit where it joins the air. This phase lasts about a minute, when the water has been stirred as rapidly as is possible by hand, and then it will be noticed that *pulsations* set in: at first these are feeble, and succeed each other with great rapidity; but their period rather rapidly lengthens till it may last four seconds or more, and at the same time they become more and more violent.

The course of events during a single pulsation is as follows:—1st phase, the surface-curve of the water flattens, and in the later stages of the experiment the curvature disappears; whilst, so far as can be judged by eye and from the photographs, at the instant when the surface of the water is most nearly

level, or just before it, a column of steam springs up with great rapidity from the base of the beaker to the surface of the water, heaving this up in its central portion, and in the later stages of the experiment often causing the ejection of water from the beaker. This phase is shown in fig. 2, where the reversal of the surface curvature is very evident. Immediately after the eruption of the steam, and whilst the steam-column still stretches from the base of the beaker to the surface of the water, follows the 2nd phase. The steam-column seems to condense and breaks up, leaving only a few small bubbles, which either hang stationary or move *downwards* in the liquid; whilst if the water has dust in it the motion of the dust particles shows that

Fig. 2.



a curious kind of annular wave, concentric with the steam-column and at any moment occupying a horizontal plane, traverses the water *from top to bottom*, and spreads out in so doing, apparently causing in its course the partial or almost complete condensation of the steam and the curious brief *downward* movement of the bubbles left: at the same time the surface of the water in the beaker becomes deeply indented, perhaps sinking in to take the place of the steam which has condensed, (though the writer does not feel at all certain that this is the

Fig. 3.

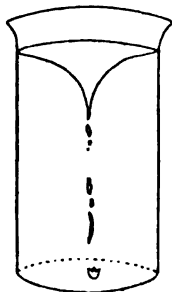
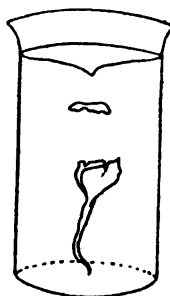


Fig. 4.



cause of the depression formed). This second part of the pulsation is illustrated by fig. 3. After this the apex of the

surface vortex rises, and the first phase of the phenomenon recurs. This state of pulsations continues for perhaps three or four minutes: the eruptions of steam are very violent towards the close of the period, especially if the water has been boiled for long, or is made slightly alkaline (the conditions for boiling with bumping), and fig. 4 shows the effect of such a condition of things. The original photograph was taken midway through the pulsation period and in the 2nd phase. In this photograph it will be noticed that the point where the steam was first formed is not on the surface of the beaker as it generally is, but in the water itself. Some other photographs were taken at the close of the pulsation period, when the axis of rotation of the water begins to "wobble," and consequently the point where the steam is formed is not, as a rule, in the geometrical vertical axis of the beaker. Soon after this "wobbling" sets in the steam begins to be formed anywhere, at, or near, the bottom of the beaker—and all evidence of the effects of rotation vanishes.

The curve of the surface of the water throughout is never a *parabola*, as it would be if the angular velocity of the water were everywhere equal: thus the divergence from the parabolic form indicates how very much more rapidly the water rotates as it nears the axis of rotation. This fact is also evident from the inspection of the lines formed by the small bubbles rotating near the base of the steam-column as already mentioned. One might naturally expect that the outbursts of steam, (those which occur during the pulsation period), would occur when the surface vortex was deepest,—instead of which the exact opposite is the case. At times, too, large bubbles of steam form suddenly in the water and condense, without the surface-level of the water in the jar being *simultaneously* visibly disturbed: at any rate, if it be so—and it would seem that it must be, considering the high elasticity and incompressibility of water,—the disturbance is anything but easy to observe.

With respect to the cause of the pulsations already alluded to, it may be well to state that by stirring *cold* water in a beaker-shaped jar, having a small hole in its bottom through which a stream of air-bubbles can be blown (to imitate the



generation of the steam, but not its condensation), there is abundant evidence from the motion of small bubbles that pulsations set in in this case also, and indeed there is some evidence of a similar phenomenon when an ordinary glass of water is stirred: hence it does not seem likely that in the case of the hot water the pulsations are directly caused by either the formation or condensation of the steam, although this may reinforce them when once they have been set up.

Lastly, the form of the steam-columns often presents an unmistakable likeness to those of solar prominences, which can scarcely be altogether fanciful; for there is every reason to believe that the latter are explosive emissions of gaseous matter projected through and above the solar atmosphere. May not their immediate cause be the diminution of pressure on the sun's surface at and near the centre or centres of "depressions" caused by violent cyclonic disturbances in the solar atmosphere? The enormous velocity with which such ejected matter is seen to rise, and also the rapidity with which it is dispersed, have their counterparts in the experiments which have been described: no one who sees these last for himself can fail to be impressed by the great velocity with which the steam-column rises in the water, and by the suddenness with which it condenses, and that, too, in water at, or at any rate very near to, its boiling-point,—whilst the hanging filaments such as appear in fig. 3 recall most vividly some well-known drawings of solar prominences as they die out: the fact that in both cases the filaments hang with their length vertical, and do not lie horizontally, seems to the writer very significant.

This short paper is little more than a description of a phenomenon of which the writer has never seen any account given elsewhere; it makes hardly any attempt to explain much of it; still it is offered in the hope that some one more conversant with hydrodynamics than the author may give the true solutions to the questions it suggests.

Eton, Bucks, May 1902.

## DISCUSSION.

Mr. C. V. BOYS exhibited a small heat engine in which rotating water evolved steam without ebullition.

Mr. T. H. BLAKESLEY expressed his interest in the apparent want of buoyancy of the steam-bubbles in the second phase of the pulsation. He said that in filtering liquids he had sometimes noticed what appeared to be large bubbles of air which lacked buoyancy. They were really drops of the liquid surrounded by a film of air, a fact demonstrated, when the arrangement broke up, by the air forming a much smaller bubble possessing the usual signs of buoyancy. Perhaps the steam-bubbles noticed by Mr. Porter were of similar construction. He suggested that the curve of the water surface could be made parabolic by rotating the beaker and giving it a flat top. In this case the vertical distance between the highest and lowest points of the surface would be a measure of the velocity of rotation after the surface cut the flat top.

Mr. W. WATSON said that as the viscosity of water changed rapidly when nearing the boiling-point, small variations in the temperature of the liquid might alter the parabolic form of the surface. Any bubbles of steam formed away from the axis of rotation would be driven to the axis on account of the density of the water being greater than that of the steam.

Mr. PRICE said he had seen some similar experiments illustrating the formation of waterspouts. The appearance was like the effect shown, but the pulsations were absent.

Dr. A. GRIFFITHS, in suggesting an explanation of the oscillation of the water, pointed out that if the distance of a rotating body (held in position by a spring) from the axis be forcibly diminished, the conservation of the moment of momentum indicates an increased rate of rotation. On releasing the body, the increased centrifugal force causes it to shoot past its original position. Beyond the position of equilibrium, the conservation of the moment of momentum indicates a diminished speed which decreases the centrifugal force. Thus the body oscillates radially. When the water in the beaker is flat, the mass of the water is at a less average distance from the axis of rotation, than when it is heaped

towards the sides. Thus the outward-driving force is probably larger when the depression is small than when it is large. The outward force drives the water beyond the position of equilibrium which it would hold in the absence of oscillation.

Prof. S. P. THOMPSON said it would be interesting to observe the effects produced by varying the method of supplying the heat to the water.

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XXIV. *On the Heat Evolved or Absorbed when a Liquid is brought in contact with a Finely Divided Solid.* By G. J. PARKS\*.

I. INTRODUCTION.

POUILLET † discovered the fact that when a powder is put into a liquid which does not exert any solvent or chemical action upon it, there is a rise of temperature. In some of the experiments made by Pouillet with mineral substances, the rise of temperature varied from  $3^{\circ}$  to  $1^{\circ}$  C. This discovery was confirmed by several other investigators, but nearly all the earlier observations were merely thermometric, and are therefore of little value for purposes of comparison, since the rise of temperature must obviously depend on the thermal capacity of the whole mass throughout which the heat is distributed. In fact, by suitably varying the conditions of the experiment it has been found possible to obtain any rise of temperature up to  $30^{\circ}$  C. or more.

Junck ‡ found that when sand is placed in water the temperature of which is above  $4^{\circ}$  C. there is a rise of temperature, and when the temperature of the water is below  $4^{\circ}$  C. there is a fall of temperature. This is quite in accordance with what would be expected on the supposition that the *Pouillet effect* is due to a pressure at the surface of the powder,

\* Read June 20, 1902.

† Pouillet, *Ann. de Chim. et de Physique*, xx. p. 141 (1822).

‡ Junck, *Pogg. Ann.* cxxv. p. 292 (1865).

and the variation of pressure for a given variation of temperature can be calculated from the equation  $dp = \frac{J.c.\rho}{\tau \cdot \alpha} d\tau$ , where  $\alpha$  is the coefficient of expansion of the liquid at constant pressure,  $\rho$  the density,  $c$  the specific heat,  $\tau$  the absolute temperature, and  $J$  the mechanical equivalent of heat.

Meissner\* showed that when certain powders are placed in water at a temperature below  $4^{\circ}\text{C}$ ., a rise of temperature is observed, and he accordingly rejected the physical hypothesis of surface pressure, and adopted a chemical or physico-chemical hypothesis which had been advanced by Cantoni†, and which has been more fully developed by Martini‡. It has, however, been pointed out that the experiments of Meissner do not disprove the validity of the hypothesis of surface pressure, for as the pressure increases the point of maximum density of water is lowered, and at a pressure of about 200 atmospheres the point of maximum density of water is at or near  $0^{\circ}\text{C}$ ., as shown by Tait, Amagat, Lussana, and others§.

Lagergren|| has shown that the pressure at the surface of silica and water would, from the above equation, amount to some thousands of atmospheres.

Martini, on the other hand, is unwilling to admit such an enormous pressure at the surface, and he supposes that, just as some solids are dissolved by liquids and thereby become liquid, so liquids are absorbed by powders and thereby become solid, the heat evolved being equivalent to the latent heat which the liquid gives up in solidifying.

Other investigators who have made experiments on the Pouillet effect and allied phenomena are Tate¶, Melsens\*\*,

\* Meissner, *Wied. Ann.* xxix. p. 114 (1886).

† Cantoni, *Rend. del R. Istituto Lombardo*, viii. p. 135 (1866).

‡ Martini, *Atti del R. Istituto Veneto*, viii. (1896); ix. (1897); xii. (1900).

§ Tait, *Proc. Roy. Soc. Edinburgh*, 1881-82, 1882-83; Marshall, Smith & Omond, *Proc. Roy. Soc. Edinb.*, 1881-82; Amagat, *Comptes Rendus*, cxvi. p. 946 (1893); Lussana, *Nuovo Cimento* (4) ii. p. 233 (1895).

|| Lagergren, *Kongl. Vetenskaps Akademien*, B. 24, Afd. ii., Stockholm, 1899.

¶ Tate, *Phil. Mag.* [4] xx. p. 508 (1860).

\*\* Melsens, *Mémoires de l'Académie de Belgique*, xxiii. (1873); *Ann. de Chim. et de Phys.* [5] iii. p. 522 (1874).

Chappuis \*, Wiedemann and Lüdeking †, Gore ‡, Ercolini §, Bellati ||, and Linebarger ¶.

In Gore's experiments, a powder such as silica or alumina was dropped from the air into water which contained some soluble salt; the liquid was not stirred, and the temperature observed was that of the powder which sank to the bottom of the liquid. The object of these experiments was to discover the influence of the substance in solution; and in fact the whole research was the outcome of another investigation in which Dr. Gore showed that a powder has the property of abstracting from a liquid part of the substance in solution. One remark of Dr. Gore bears on the present investigation: having made observations on precipitated silica and sand, he states that the action is purely a surface one, and he suggests that if the relation between the rise of temperature and the area of the surface were known, the method could be employed to obtain the area of the surface of a powder.

Prof. FitzGerald\*\* regarded the Pouillet effect as due to a pressure at the surface of the powder and the liquid; he suggested the application of the laws of thermodynamics, and he pointed out the need of further investigation and quantitative treatment.

Notwithstanding the large number of observations which have been made in connexion with this phenomenon, there are no data by means of which we are enabled to express the quantity of heat evolved as a function of the area of the surface. The experiments of Martini, Ercolini, and others show that for the *same* powder and liquid the quantity of heat evolved is proportional to the mass of the powder used in the experiment, but no attempts have been made to calculate the area of the surface exposed to the liquid. The equation used by Ercolini is  $M + pc - \frac{p}{\theta} \cdot k = 0$ , where  $M$  is the mass of the

\* Chappuis, Wied. *Ann.* xix. p. 21 (1883).

† Wiedemann and Lüdeking, Wied. *Ann.* xxv. p. 145 (1885).

‡ Gore, Phil. Mag. xxxvii. p. 306 (1894); Birm. Phil. Soc. Proc. vol. ix. pt. 1 (1893).

§ Ercolini, *Nuovo Cimenti*, Serie 4, vol. ix., Feb. 1899.

|| Bellati, *Atti del R. Istituto Veneto*, Tomo lix. Parte Seconda, 1900.

¶ Linebarger, *Physical Review*, vol. xiii. No. 1, July 1901.

\*\* FitzGerald, 'Nature,' vol. xlix. pp. 293, 316 (1894).

water, including the water equivalent of the calorimeter,  $p$  is the mass of the powder, and  $c$  the specific heat of the powder,  $\theta$  is the observed rise of temperature,  $k$  is a constant and represents the amount of heat evolved on putting one gram of the powder into water.

The value of  $k$  is, however, not really constant, but diminishes very slightly as  $p$  increases. Martini explains this on the supposition that some of the water is solidified on the powder and its specific heat is thereby reduced to  $\cdot 5$ . Ballati has, however, shown by direct experiment that this supposition is wrong. Some silica was well dried, and then exposed to aqueous vapour so that it absorbed moisture, the mass of which was determined by weighing the silica before and after its exposure; the specific heat of the water was then found by means of a Bunsen's ice-calorimeter, an assumed value being taken for the specific heat of silica. The specific heat of the water was found to be much greater than  $\cdot 5$ , and it did not differ very much from 1.

It seems highly probable that the specific heat of the water close to the surface of the silica differs from the specific heat of the water which is farther away from the surface, but any attempt to distinguish clearly between the two must necessarily lead to some doubtful assumptions. A consideration of the Pouillet effect is, however, incomplete if the possibility of such a variation in the specific heat of the liquid is not taken into account. There is also another possible source of variation in the quantity of heat evolved, which none of the investigators have considered, namely, the variation of the heat evolved with the temperature. In many of the records of experiments the initial temperature of the calorimeter is not even stated, and in other cases, where the temperatures are recorded, it is impossible to decide whether the variations in the quantity of heat evolved depend upon differences in the initial temperature of the liquid and powder, or upon change of specific heat of the liquid, or upon some cause of error in the experiment.

The objects of the present investigation were to obtain a relation between the quantity of heat evolved and the area of the surface exposed, to find the rate of variation of heat

evolved with variation of temperature, and to apply to the results the laws of thermodynamics.

The nearest approach to a relation connecting the quantity of heat evolved with area of surface is the statement of Mr. Linebarger, that the finer the powder the greater the heat effect, and in the case of water and silica the heat effect is about proportional to the fineness of the powder. This conclusion is based upon a very few experiments with two samples of silica of different degrees of fineness, and it is directly opposed to the views of Martini, who states that the fineness of the powder does not influence the result to any important extent\*.

## II.

### *On the Relation between the Area of Surface of Silica and the Heat evolved on bringing the Surface in contact with Water.*

In making any experiment on the Pouillet effect, it is essential that the powder should be perfectly dry and that it should be at exactly the same temperature as the liquid. Very few of the investigators have succeeded in securing these conditions, but Mr. Linebarger's methods seem to leave nothing to be desired, and the experiments now to be described were made in a similar way.

The precipitated silica, sand, or other substance to be experimented upon, was heated in an evaporating dish to dull red-heat. A test-tube was drawn out to a narrow neck at about seven or eight centimetres from the closed end, and the tube was then weighed. Some of the powder was now placed in the tube while it was still hot, and the tube was connected to an air-pump, and the air was exhausted as completely as possible, the powder being at the same time heated until the tube showed signs of softening and closing in under the atmospheric pressure. The bulb was now sealed at the narrow neck, and when cold the whole of the tube and the

\* Martini, *Atti del R. Istituto Veneto*, Tomo lix. Parte Seconda (1900), p. 622 (Non è dunque la sottigliezza dei granuli della polvere che influisca in modo sostanziale sul fenomeno come ce lo provano le tre qualità di carbonato di calce).

powder were weighed together ; the difference between this weighing and the first weighing gave the mass of the powder, and a third weighing gave the mass of bulb and powder.

The calorimeter used in these experiments was a copper vessel, 9 cm. in height and 7.5 cm. in diameter ; it weighed 104.605 grammes, and its water equivalent was 9.95 grammes. This was suspended by silken threads inside another copper vessel, this again was placed in a glass beaker containing water, and the glass beaker was placed inside another glass beaker, the space between the two beakers being filled with "glass wool" or "cotton silicate," which is a very bad conductor of heat. The whole apparatus was kept in a cupboard with glass doors. The temperature of the calorimeter could therefore be kept constant for a considerable time.

The thermometers were divided to  $\cdot 02^{\circ}$  C., and the readings were taken to the tenth of a division, so that there was a possible error in each reading of not more than  $\cdot 002^{\circ}$  C.

An instrument was used to serve the purpose of crushing the bulb, thus liberating the powder under the surface of the water, and it also served as a stirrer to keep the temperature of the water uniform. A piece of brass tubing about an inch in diameter was filed away in the middle, thus leaving two rings at the ends about an inch apart and connected by that part of the tube between them which had not been filed away. A nut was soldered on to the tube between the rings and a screw worked in the nut, the axis of the screw being at right angles to the axis of the tube, so that when the glass bulb was placed in the tube it was held firmly by the screw pressing against it, and a few more turns of the screw were sufficient to break the bulb. The top of the screw was flattened to a sharp edge, which engaged in a split at the end of a stout brass wire ; this wire could thus be used to turn the screw, and then could be immediately removed. A piece of glass tubing was attached to the brass tube so that the screw worked along the axis of the glass tube, which served as a handle of non-conducting material. The water equivalent of this instrument was 2.35 grammes, and that of each thermometer was 1.50 grammes.

In making an experiment, the bulb containing the powder was placed under the surface of the water in the calorimeter,



and allowed to remain there for some hours, generally about twenty-four hours. The temperature was then observed every five minutes, and if several consecutive readings were the same, the bulb was broken, and the temperature again observed until it was constant. The rise of temperature was generally complete in three minutes or less, the liquid being gently stirred together with the powder.

The mass of water,  $M$ , was always large compared with the mass of the powder,  $p$ , and hence the error, if any, involved in taking the specific heat of the water as 1, must have been exceedingly small. The temperatures at which the experiments were made did not differ very much, and the variation due to these small differences of temperature was neglected; from theoretical considerations it follows that the variation in the heat evolved is not more than .3 per cent. per degree centigrade, and later experiments tend to confirm this.

The specific heat of the glass bulb and its contents was taken as .19; any error in this assumption could not have affected the results, since the mass of the bulb and its contents was always small compared with the mass of water.

The average diameter of the grains of powder was obtained by measuring many hundreds of grains by means of a microscope supplied with stage micrometer and eyepiece micrometer. The microscope was so adjusted that thirty divisions of the eyepiece micrometer exactly corresponded to one tenth of a millimetre on the stage micrometer, so that one division of the eyepiece micrometer represented  $\frac{1}{3000}$  cm. It was found that in the dry state the smaller grains of powder were often joined together, forming larger grains, and it was not easy to distinguish a lump consisting of several small grains from a complete grain; hence any measurements of powder in the dry state are likely to make the powder appear much coarser than it really is. When the powder was put in a drop of water on a glass slide under the microscope and stirred with a small brush, the larger pieces of silica were seen to break up into smaller grains of fairly uniform size. The average diameter of the grains was found to be  $\frac{1}{4}$  of a division of the eyepiece micrometer, that is .00025 cm. Suppose now there are  $n$  such average grains to a gramme of powder, then, since the specific gravity of the

powder is 2.2, we have

$$n \times \frac{\pi}{6} (\cdot 00025)^3 \times 2.2 = 1$$

on the assumption that the grains are spherical, and the area of surface is equal to

$$n \cdot \pi (\cdot 00025)^2 = 6 \times \frac{1}{2.2} \times \frac{1}{\cdot 00025} = 10900 \text{ sq. cm.}$$

That is, one gramme of the precipitated silica exposed a surface of about 10900 sq. cm. Another variety of silica used in these experiments was examined under the microscope, and the average diameter of the grains was found to be 1.2 divisions or  $\cdot 00040$  cm., so that the area of surface per gramme was

$$6 \times \frac{1}{\cdot 0004} \times \frac{1}{2.2} = 6820 \text{ sq. cm.}$$

Experiments were also made with some fine grey sand of specific gravity 2.6; the average diameter of the grains was  $\cdot 010$  cm., and the area of the surface exposed by one gramme of the sand was therefore

$$6 \times \frac{1}{2.6} \times \frac{1}{\cdot 01} = 231 \text{ sq. cm.,}$$

on the assumption that the grains were spherical.

The probable error in estimating the surface of a powder by this method is considerable, because the particles are irregular in shape and size, especially those of the sand. Experiments were therefore made with "cotton silicate" or "glass wool," a kind of glass of specific gravity 2.7, in the form of fine filaments which, when examined under the microscope, are seen to be almost perfect cylinders, of fairly uniform size. The length of each cylindrical filament was very great compared with its diameter, so that in calculating the area of its surface only the curved surface was considered. The average diameter was found to be  $\cdot 00175$  cm.; hence the area of surface exposed by one gramme of the silicate was

$$\frac{4}{2.7 \times \cdot 00175} = 847 \text{ sq. cm.}$$

The accompanying table (I.) shows the results of some of the experiments. Other experiments were made, but the results are not shown because they are considered to be unreliable. In several experiments, there was a slight crack in the bulb before it was placed in the calorimeter, and in these instances the result obtained was far too low, though the crack was not large enough to admit any visible quantity of water; this shows the great importance of keeping the powder dry until the moment of the experiment. Other experiments were rejected because there was a rapid variation in the temperature of the room at the time, so that the final temperature of the calorimeter did not reach a constant value until long after the time usually occupied in making an experiment. The rise of temperature observed in the experiments with sand and cotton silicate was only about  $\frac{1}{2}^{\circ}\text{C}.$ , and hence the results are only given to the second significant figure.

TABLE I.

Number of Experiments.	Nature of Substance.	Diameter (cm.).	Estimated area of surface per gramme.	Mass of substance in grammes.	Mass of bulb.	Mass of water including water-equivalent of calorimeter, powder, bulb, thermometer, and stirrer.	Initial Temperature (Centigrade).	Rise of Temperature.	Calories per gramme of the substance.	Calories per sq. cm. of the surface.
1.	Silica (precipitated)	00025	10900	3.749	3.34	205.51	6.334	.208	11.4	00105
2.	" "	"	"	3.563	3.55	210.31	6.552	.192	11.3	00104
3.	" "	"	"	4.169	3.61	210.05	7.012	.222	11.2	00103
4.	" "	"	"	4.037	3.53	239.74	7.586	.194	11.5	00105
5.*	" "	00040	6820	3.940	4.03	207.26	7.320	.136	7.15	00105
6.	Sand	.010	231	20.050	3.70	220.03	5.400	.022	.24	0010
7.	"	"	"	20.589	4.67	240.10	5.482	.020	.23	0010
8.	"	"	"	22.033	3.81	252.28	8.320	.020	.23	0010
9.	"	"	"	20.188	4.14	255.15	9.228	.018	.23	0010
10.	Silicate (cylindrical filaments)	00175	847	2.240	3.81	200.10	5.742	.010	.89	0011
11.	" "	"	"	4.006	3.50	210.98	5.722	.018	.95	0011
12.	" "	"	"	4.138	3.47	211.75	6.052	.018	.92	0011

\* See Table II. for results of other experiments with silica.

It is considered that these results justify the enunciation of the following law :—

*When silica, sand, or glass, is brought in contact with water, at approximately constant temperature, the heat evolved is proportional to the area of the surface exposed by the solid, and the amount of heat developed per square centimetre is approximately .00105 calorie when the temperature is near 7° C.*

### III.

#### *Application of the Laws of Thermodynamics.*

Assuming that the phenomenon of Pouillet is reversible, we may apply the laws of thermodynamics. Let  $h$  be the amount of heat developed per square centimetre at the surface of the solid and liquid at constant temperature, let  $c$  be the specific heat of the liquid when the surface remains constant, let  $s$  be the area of surface of the powder exposed to one gramme of the liquid, the volume of which is supposed to remain constant, let  $P$  be the surface-pressure for the given solid and liquid. Then, with the usual notation of thermodynamics,

$$dQ = c \cdot dt - h \cdot ds, \quad . . . . . (i.)$$

and  $dQ = \tau \cdot d\phi$ , hence

$$\tau \cdot d\phi = c \cdot dt - h \cdot ds. \quad . . . . . (ii.)$$

The variation of the internal energy is

$$dU = J \cdot dQ - P \cdot ds = J \cdot c \cdot dt - (J \cdot h + P) ds, \quad (iii.)$$

where  $J$  represents the mechanical equivalent of heat. Imposing the condition that the variation of the internal energy is a perfect differential, we obtain

$$J \left( \frac{dc}{ds} + \frac{dh}{dt} \right) = - \frac{dP}{dt}. \quad . . . . . (iv.)$$

Imposing the condition that the variation of entropy,  $d\phi$ , is a perfect differential, we obtain

$$\frac{dc}{ds} + \frac{dh}{dt} = \frac{h}{\tau}. \quad . . . . . (v.)$$



TABLE II.

Experiments with precipitated Silica. Average diameter of grains .00040 cm. Estimated area of surface per gramme 6820 sq. cm.

Number of Experiment.	Mass of powder in grammes.	Mass of bulb.	Mass of water, including water-equivalent of calorimeter, powder, bulb, thermometer, and stirrer.	Initial Temp. (Cent.).	Rise of Temperature.	Calories per gramme of powder.	Calories per sq. cm. of surface.
1. ....	3.940	4.03	207.26	7.320	.136	7.15	.00105
2. ....	4.282	3.32	190.26	7.300	.164	7.29	.00107
3. ....	3.760	3.55	201.88	6.930	.134	7.19	.00105
4. ....	3.602	3.25	195.71	6.238	.132	7.17	.00105
5. ....	3.721	4.00	196.26	6.770	.136	7.17	.00105
6. ....	3.601	3.32	211.49	7.200	.122	7.17	.00105
7. ....	3.256	3.58	205.25	7.106	.114	7.19	.00105
8. ....	4.166	3.74	214.16	7.502	.138	7.09	.00104
9. ....	4.261	4.14	197.01	23.636	.164	7.58	.00111
10. ....	3.950	3.92	182.94	24.180	.162	7.50	.00110
11. ....	3.657	3.22	202.57	24.410	.138	7.64	.00112
12. ....	4.789	4.67	206.67	24.000	.178	7.68	.00113
13. ....	4.417	3.79	212.02	24.060	.160	7.68	.00113
14. ....	4.691	3.17	230.80	24.670	.154	7.58	.00111
15. ....	4.003	3.84	227.21	23.906	.130	7.38	.00108
16. ....	3.829	2.99	227.68	24.700	.124	7.37	.00108

It was found necessary to modify the apparatus so that the calorimeter could be kept for some hours at constant temperature above that of the atmosphere. The cylindrical copper vessel in which the calorimeter was suspended was closed by a tightly fitting copper lid, under the rim of which was tightly packed an indiarubber ring which had previously been stretched around the top of the vessel. Into the copper lid, two copper tubes about two inches long were soldered; through one of these tubes the bulb of the thermometer could be put into the calorimeter, and through the other passed the handle of the crushing instrument. Thus the bulb could be crushed and the liquid stirred and the temperature observed without opening the vessel. The copper vessel was now immersed in several gallons of water, the top of the lid being about an inch below the surface. This water was kept at

approximately constant temperature for several hours, during which time the bulb containing the powder was immersed in the water in the calorimeter, so that there could be no doubt about the powder and the water being at the same temperature.

This apparatus proved so satisfactory that it was finally adopted in the later experiments at the lower temperature, instead of the arrangement previously described.

In the first eight experiments the mean temperature was about  $7^{\circ}\cdot 1$  C. and the mean heat evolved was  $7\cdot 18$  calories per gramme, or  $\cdot 00105$  calorie per sq. cm. In the last eight experiments, the mean temperature was about  $24^{\circ}\cdot 3$  C. and the mean heat evolved was  $7\cdot 55$  calories per gramme or  $\cdot 00111$  calorie per sq. cm.

$$\text{The mean value of } \frac{dh}{dt} = \frac{\cdot 00006}{17\cdot 2} = \cdot 0000035.$$

$$\text{The mean value of } \frac{h}{\tau} = \frac{\cdot 00108}{288\cdot 7} = \cdot 0000037.$$

Hence, roughly speaking,  $\frac{dh}{dt} = \frac{h}{\tau}$  and  $h$  varies as  $\tau$ , that is the heat evolved is roughly proportional to the absolute temperature.

## V.

### *On the Rate of Variation of the Specific Heat of Water with Extension of the Water-Silica Surface.*

It has been shown that  $\frac{dc}{ds} = \frac{h}{\tau} - \frac{dh}{dt}$ , and hence from the results stated above it follows that  $\frac{dc}{ds}$  must be very small. If the values of  $\frac{dh}{dt}$  and  $\frac{h}{\tau}$  are correct to the second significant figure the value of  $\frac{dc}{ds}$  is  $2 \times 10^{-7}$ , and this may be taken as indicating the order of magnitude of the term  $\frac{dc}{ds}$ .

For an accurate determination of  $\frac{dc}{ds}$ , experiments would have to be made over a much wider range of temperature, and it would be advisable also to obtain, if possible, a silica of much finer and more uniform quality than that used in these experiments.

It is known that the surface-tension of a liquid in contact

with air can be represented approximately as a linear function of the temperature, and hence, from equation (vii.),  $\frac{dc}{ds}$  is approximately zero. But it cannot be assumed that the surface-pressure of water and silica follows the same law as the surface-tension of a liquid in contact with air.

In making any experiment to determine directly the specific heat of water in contact with silica, we are met at once with the difficulty that the specific heat of silica is not accurately known.

According to Joly\* the specific heat of amorphous silica is .2375, but it has been suggested† that this value is too high, and that the error arose through neglect of the Pouillet effect; a similar question in regard to the specific heat of carbon has been investigated by Kopp, Wüllner & Bettendorf, and Weber‡.

Bellati§, in his attempt to determine the specific heat of moisture absorbed by silica, took for the specific heat of the silica the value .1993 as the mean of the various values obtained for different forms of silica.

The value of  $\frac{dc}{ds}$  cannot, however, be obtained by direct experiments such as those made by Bellati. Suppose, for example,  $p$  grammes of silica having a specific heat  $k$ , and  $w$  grammes of water, are mixed and raised to a temperature  $t$ , and the mixture is then put into a Bunsen's ice calorimeter and cooled to  $0^\circ \text{C.}$ , the heat given up is

$$\left( pk + w + p \cdot s \cdot \frac{dc}{ds} - p \cdot s \cdot \frac{dh}{dt} \right) t = \left( pk + w - p \cdot s \cdot \frac{h}{\tau} \right) \cdot t,$$

approximately, from equation v.

It is necessary, therefore, to distinguish between the *true* or *absolute* variation and the *apparent* variation in the specific heat of water in contact with a solid. The *true* variation in the specific heat is proportional to  $\frac{dc}{ds}$ , and is probably very small; but since in any experiment it is impossible to prevent

\* Joly, Proc. R. Soc. xli. p. 250 (1886).

† Martini, *Atti del R. Istituto Veneto*, Tomo lix., Parte seconda, p. 637.

‡ Weber, *Pogg. Ann.* t. 154, pp. 367-423 (1875).

§ Bellati, *Atti del R. Istituto Veneto*, Tomo lix., Parte seconda, p. 945.



the evolution or absorption of heat at the surface depending on the term  $\frac{dh}{dt}$ , the *apparent* variation in the specific heat, that is, the variation actually observed in any experiment, is proportional to the difference of the terms  $\frac{dc}{ds}$  and  $\frac{dh}{dt}$ , that is, approximately proportional to  $\frac{h}{\tau}$ .

Hence the *apparent* specific heat of water in contact with a solid is approximately  $\left(1 - \frac{A}{w} \cdot \frac{h}{\tau}\right)$ , where  $A$  is the area of the surface of the water in contact with the solid, and  $w$  the mass of the water. For example, in the earlier experiments of the present investigation, the mass of water was about 200 grammes and the area of surface exposed by 4 grammes of powder was  $4 \times 10900 = 43600$  sq. cm., and the value of  $\frac{h}{\tau}$  was  $37 \times 10^{-7}$ : hence the *apparent* specific heat of the water was equal to  $\left(1 - \frac{43600}{200} \times 37 \times 10^{-7}\right) = .99919$ . It is evident that if the mass of water is small compared with the mass of powder, the variation in the apparent specific heat may be very great, so that it is not necessary to assume, as Martini did, that some of the water is solidified on the surface of the powder, in order to account for the apparent variation in the specific heat.

## VI. *Experiments with Mercury.*

Experiments were made to show a *fall* of temperature on putting a finely divided solid into mercury. After several fruitless attempts with silica, the following method was adopted.

About 3000 grammes of mercury were placed in a glass beaker, and some cotton silicate was placed in the same beaker above the mercury; above the cotton silicate was a cardboard disk which covered the silicate entirely, except that a space was left for the insertion of the thermometer, and a little space was allowed for the edge of the disk to clear the sides of the beaker. On pressing down the disk the cotton silicate was suddenly immersed in the mercury, and in some experiments there was a fall of temperature amounting to  $.016^\circ$  C. But the results were not consistent,

for in other experiments there was a slight rise of temperature, caused probably by the cotton silicate being at a higher temperature than the mercury. After leaving the cotton silicate immersed in the mercury for some time, so as to take the same temperature, it was suddenly released, and a rise of temperature was the invariable result. With 11 grammes of cotton silicate the rise of temperature was about  $.02^{\circ}\text{C.}$ , and with 30 grammes of silicate the rise of temperature was about  $.05^{\circ}\text{C.}$ , but the results varied considerably.

These experiments do not lend themselves to quantitative measurement, for the surface of the mercury cannot be determined. When the filaments of cotton silicate are put into mercury they tend to cling together in bundles or tufts, and the mercury breaks up into a great number of little globules between the tufts of silicate. The surface exposed by the mercury is thus large and indeterminate. The results show, however, that the sudden contraction of a mercury surface causes an evolution of heat and corresponding rise of temperature, and the effect can be regarded as a modification of the Pouillet effect for a liquid which does not *wet*, or enter into intimate contact with the solid.

H.M. Dockyard School, Portsmouth,  
March 1902.

#### DISCUSSION.

Prof. EVERETT said the research was a valuable contribution to our knowledge of the Pouillet effect. The results were consistent in showing a generation of heat to the amount of about one-thousandth of a therm per sq. cm. of increase of surface of contact between the water and the silica. He thought this heat must be due to diminution of volume in the water-film; for extension of area of a liquid film tended to produce cold. Cold was in fact produced by enlargement of the surface of mercury in the concluding experiments.

Mr. J. MACFARLANE GRAY said that the paper was to him peculiarly interesting, because satisfactory explanations of the phenomena described could be obtained by substituting the universal dynamic pressure of a corpuscular ether for the unthinkable universal attraction of matter. He gave an example to illustrate what he calls the metafilm at a surface,

and pointed out that it is necessary to consider both the matter-volume and the meta-volume of bodies to get at the explanation of physical phenomena. In the Author's experiments there is a diminution of meta-volume, and the ether produces heat equal to the product of the ether pressure and the volume of the cancelled metafilm, just as the heat of evaporation is reproduced when steam is condensed. The experiments were to him not a surprise, but a confirmation of his views.

Mr. J. H. GARDINER drew attention to the necessity of heating the powdered silica to red heat in order to get rid of moisture. If possible, the silica should be heated in the actual tube and sealed up whilst hot.

Mr. R. S. WHIPPLE said that Dr. Cobbett had shown that results very similar to the Pouillet effect could be obtained with an ordinary clinical thermometer and a piece of muslin. The bulb of the thermometer was covered with two or three layers of muslin, and the thermometer, thus covered, was placed inside a sterilizer which was maintained at the normal blood temperature,  $98^{\circ}4$  F., for several hours. If the thermometer, still covered with muslin, was then placed in the mouth of a person whose temperature was normal, a rise of two or three degrees would be shown by the thermometer.

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XXV. *On a Remarkable Case of Uneven Distribution of Light in a Diffraction Grating Spectrum.* By R. W. WOOD, *Professor of Experimental Physics, Johns Hopkins University*.\*

It is a well-known fact that in the spectra formed by a diffraction-grating the light is unevenly distributed, that is the total light in any one spectrum will not recombine to form white light.

I have been examining a most remarkable grating recently ruled on one of the Rowland dividing-engines in which this uneven distribution is carried to a degree almost incomprehensible. If the spectra of an incandescent lamp are viewed

\* Read June 20, 1902.

directly in the grating without any other optical appliance, at certain angles of incidence perfectly sharp monochromatic images of the filament appear in different parts of the first order spectra. Sometimes these images are nearly black, and sometimes they are far brighter than the rest of the spectrum. On mounting the grating on the table of a spectrometer I was astounded to find that under certain conditions the drop from maximum illumination to minimum, a drop certainly of from 10 to 1, occurred within a range of wave-lengths not greater than the distance between the sodium lines. *In other words, this grating at a certain angle of incidence will show one of the D lines, and not the other.*

Setting the grating at nearly normal incidence, a bright narrow line appeared in the yellow, and a slightly broader dark line showed up in the green. On decreasing the angle of incidence these lines approached one another, one travelling up the spectrum, the other down. At an incidence angle of a few minutes they came in contact, presenting an appearance very similar to one of the shaded lines in the spectrum of a Nova. On decreasing the angle of incidence to zero, the lines fused producing uniform illumination at the spot.

When the light is incident on the opposite side of the normal from the spectrum we find the red and orange extremely brilliant up to a certain wave-length, where the intensity suddenly drops almost to zero, the fall occurring, as I have said, within a range not greater than the distance between the D lines. A change of wave-length of  $1/1000$  is then sufficient to cause the illumination in the spectrum to change from a maximum to a minimum.

The theory of the diffraction-grating, as it stands at the present time, appeared to me to be wholly inadequate to explain this most extraordinary distribution of light, and I accordingly endeavoured to find out if possible the necessary modifications which must be introduced.

The ordinary theory shows that under certain conditions (square groove and normal incidence for example) the directly reflected light, or central image, may have certain wave-lengths wholly absent and appear strongly coloured in consequence. Coloured central images have been studied experimentally by Quincke, and Rayleigh has treated them

theoretically for transmission-gratings, and Rowland for gratings acting by reflexion.

In studying the colours of these central images I have found that when the plane of polarization is parallel to the groove the colour is quite different from what it is when the plane is at right angles to the groove. The polarizing power of gratings has been experimentally investigated by Wien and Rubens, but to the best of my knowledge their experiments were confined to wire gratings, and dealt merely with the amount of light directly transmitted under the two conditions. So far as I know, polarization has never been introduced into the theory of gratings.

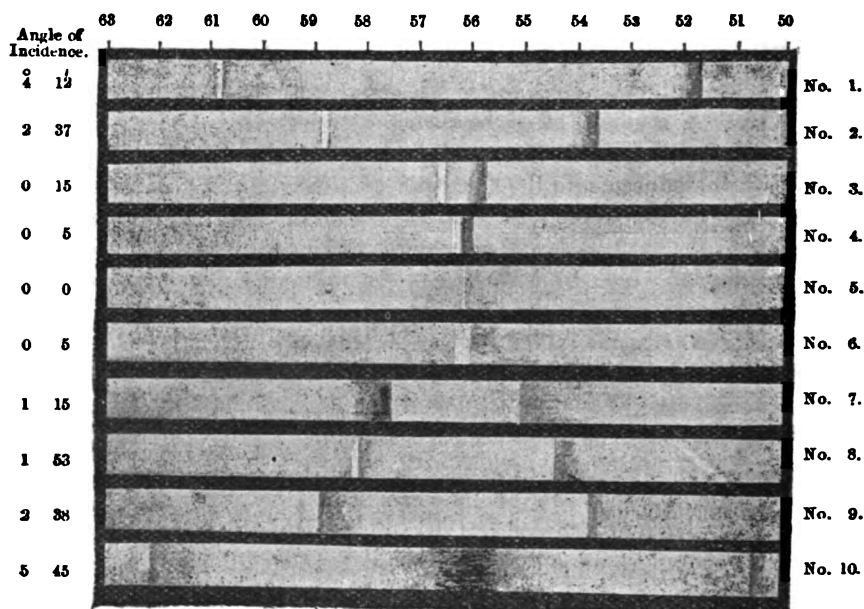
It occurred to me that polarization might prove to be the key to the explanation of the very singular behaviour of the grating of which I am writing. Experiment proved this to be the case, for it was found that *the singular anomalies were exhibited only when the direction of vibration (electric vector) was at right angles to the ruling*. On turning the nicol through a right angle all trace of the bright and dark bands disappeared. The bands are naturally much more conspicuous when polarized light is employed.

We will now examine in some detail the appearance of the spectrum at different angles of incidence. In fig. 1 we have the appearance of the spectrum for ten different angles of incidence. The position of the dark and light bands in the spectrum was determined by employing sunlight, and using the Fraunhofer lines as reference-marks. The wavelengths are indicated at the top of the figure, and the angles of incidence at the left. Beginning with No. 1, we have the light incident at an angle of  $4^{\circ} 12'$  on the same side of the normal as the spectrum. A bright line not much wider than the distance between the D lines appears at wave-length 609, and a dark band at 517 : the latter is sharp and black on one side and shades off gradually on the other. On decreasing the angle of incidence to  $2^{\circ} 37'$  the bands approach, occupying the positions shown in No. 2.

Numbers 3 and 4 show two subsequent positions, and it will be noticed that the rate of progress along the normal spectrum is the same for each. In No. 4 we have the appearance which I have likened to the line in the spectrum of a Nova.

In No. 5 the incidence is normal and the lines have fused and disappeared. This is not merely an approximation, for I have found that if the grating be turned until the spectrum has this appearance, the light reflected back through the

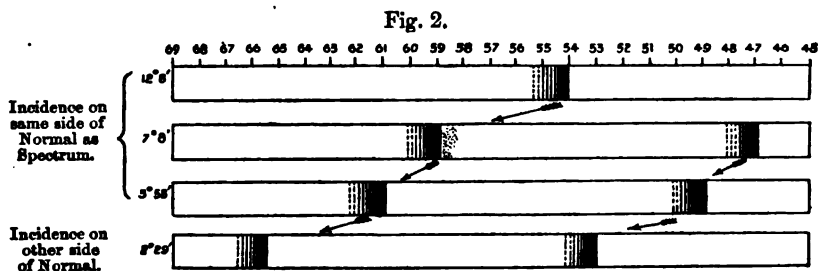
Fig. 1.



collimator passes through the slit. This furnishes us with a new method for adjusting a grating for normal incidence. On passing this position a narrow bright line appears which broadens into a very sharply defined rectangle, appearing, as is shown in No. 6, at an incidence angle of  $5'$  on the opposite side of the normal from the spectrum. This rectangle broadens as the angle of incidence increases, its edges becoming heavily shaded, as is shown in No. 7, where we have essentially two dark bands retreating from each other at equal rates as the angle of incidence increases. There is nothing especially peculiar about the one which is journeying towards the violet end of the spectrum, but the other behaves in a most singular manner, which could only be fully illustrated by a kinematograph-view of its changes. In No. 7

we find it very sharp and black on the right-hand edge, shading off towards the red end of the spectrum. As it moves along, a shadow appears on its right-hand side, the two shadows being separated, however, by a narrow bright region; the right-hand shadow increases in depth, while the left-hand one clears up, until the band becomes symmetrical, a narrow bright line with a shadow on each side, as is shown in No. 8. On increasing the angle of incidence still further, the inverse of this operation takes place, until in No. 9 the shadow has transferred its position to the right, and appears with a sharp black edge as before only reversed in position. This process of turning inside out of the shadow marks the beginning of another curious event, for, as the reversed shadow travels along towards the red with increasing angle of incidence, an exceedingly black symmetrical band splits off from it and travels down the spectrum in the opposite direction, arriving at the position shown in No. 10, at an incidence angle of  $5^{\circ} 45'$ . This band is much wider than the others and seems to be absolutely black at the centre, even with a fairly wide slit.

This represents the cycle when the grating is in air. If a piece of plane-parallel glass is cemented to the front of the grating with cedar oil the cycle is quite different. In this case we have a pair of unsymmetrical shaded bands which move in the same direction as the angle of incidence is changed. In fig. 2 I have given the appearance and position

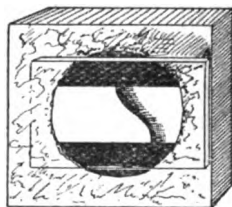


of these bands for three different angles of incidence. It will be observed that they remain distinct on passing through the position of perpendicular incidence.

It is impossible to identify these bands with those observed

with the grating in air, since the jump in the refractive index of the medium in which the grating is immersed is too great. To determine the effect of increasing the refractive index of the medium on the position of a given band I fastened a plate of glass in front of the grating at a distance of about 0.3 mm. from the ruled surface. Water was introduced between the two, and glycerine applied to the lower edge. The denser fluid gradually diffused up into the water, and I observed the dark bands sharply curved, on looking at the spectrum directly in the grating without the aid of a telescope, the shift being towards the red, as the refractive index increased. The appearance of one of the bands is shown in fig. 3. It will be observed that the shift is in the same direction as when a resonator is immersed in a medium of high dielectric constant, and though there may be no connexion between the two phenomena, it seems perhaps worth while to mention it as there may be something akin to resonance in the action of this grating.

Fig. 3.



It is useless to attempt to fully explain the very complicated sequence of events which I have outlined, until some working hypothesis is established which will explain some one of them, and it appears to me that the first thing to do is to make some assumption which will explain the very remarkable fact that a change of wave-length of one part in a thousand is sufficient to change the illumination from a maximum to a minimum.

We know that this can take place if we are dealing with interference with a large difference of path. Hamy's "extincteur"\* is a piece of apparatus which illustrates this better than anything with which I am familiar. It occurred to me that possibly the anomalies were to be referred in some way to the interference between disturbances coming from widely separated lines, though I had no very definite idea as to just how it could produce any of the anomalies, or how it was to be connected with the polarization effect. It seemed worth while, however, to investigate the matter, and

\* M. Hamy, *Compt. Rend.* cxxv. p. 1002 (1897).



I accordingly covered the grating with a thin sheet of black paper, leaving exposed only a strip about 0.3 mm. wide along one edge. By bringing the eye close up to this small strip the spectrum could be distinctly seen, but the sharpness of the dark bands seemed to be undiminished. As there were only about 200 lines acting there could not have been any very considerable difference of path between even the extreme rays. In consequence of this I am compelled to refer the matter to the form of the groove. The important fact which must be taken into account in any endeavour to explain the action of the grating is, that the anomalies only occur when the electric vector lies across the ridge. We can speculate about the action of the narrow ridges on the light waves, assuming, perhaps, something of the nature of resonance taking place across the ridge, or we can seek for the explanation in the behaviour of the transverse vibrations in between the ridges, but in any case we are confronted with the difficulty of explaining the tremendous change in the intensity of the illumination with the exceedingly small change of wave-length.

The study of this grating has been limited to the two or three days immediately preceding the closing of the laboratory for the summer, consequently I have been unable to give a very exhaustive account of its behaviour under other conditions, or secure any very satisfactory photographs of the peculiar spectra. The few photographs which I have taken and which are reproduced, were made on some old orthochromatic plates, without any especial appliances, the plates being applied to the end of the spectrometer tube, while the slit was illuminated with a Nernst lamp, which makes the best source of light possible when a continuous spectrum is required. The photographs are interesting as showing the sharpness of the bright and dark bands in the spectrum. I am of the opinion that a study of the colours of the central image with polarized light in the case of this grating may throw some further light on the problem, which is one of the most interesting that I have ever met with.

Baltimore, June 2nd, 1902.

XXVI. *On the Electrical Resonance of Metal Particles for Light-Waves—Second Communication.* By R. W. WOOD, *Professor of Experimental Physics, Johns Hopkins University*\*.

IN a previous paper† I have shown that granular deposits of the alkali metals exhibit brilliant colours by transmitted light. These colours were referred provisionally to the electrical resonance of the minute particles for light-waves.

At the time of writing this paper, I was not acquainted with Prof. Threlfall's interesting work on the optical properties of metallic precipitates and his attempts to verify the polarization effects calculated by Prof. Thomson, to which I alluded. I feel sure that the colours observed by Prof. Threlfall, and those which I have observed, are to be referred to the same causes. It was found that the immersion of the particles in a liquid of high dielectric constant produced striking changes in the colour of the transmitted light, the change corresponding to a shift in the absorption-band towards the red end of the spectrum. It has been recently shown by Aschkinass and Shaefer‡ that the length of electromagnetic waves to which a system of metallic resonators respond, is increased by immersing the resonator system in a liquid of high dielectric constant, which is obviously analogous to the behaviour of the sodium and potassium films. It is also well known that the position of the absorption-band of aniline dyes depends to a certain extent on the dielectric constant of the medium in which the dye is dissolved.

Continued investigation along the lines indicated in my previous paper has convinced me that it is impossible to refer the colours either to interference or diffraction, and it remains only to determine whether the resonance of the metal films is molecular, as in the case of the aniline dyes, or whether we are dealing with an electrical vibration of metallic masses, smaller than the light-waves though of the same order of magnitude. At the time of writing my first paper

\* Read June 20, 1892.

† Proc. Physical Society, vol. xviii. p. 166; Phil. Mag. April 1902.

‡ Drude's *Annalen der Physik*, vol. v. p. 489.

I had been successful in producing coloured films only with sodium, potassium, and lithium. Consequently, the only optical investigations that could be made were such as could be adapted to films formed on the walls of exhausted bulbs. Determinations of dispersion were practically impossible under these conditions, except by means of very elaborate apparatus, which it did not seem worth while to construct until further efforts had been made to obtain films of this nature which would be permanent in air, and could be examined with the interferometer. I have since succeeded in producing deposits of gold, which exhibit colours very similar to those shown by the potassium films. The deposit is formed by the discharge from a gold cathode in a moderately high vacuum, the colour depending on the distance of the glass plate from the electrode and the degree of exhaustion. Under certain conditions a green film is deposited, of a tint similar to that of gold leaf, while under other conditions blue, violet, and purple films can be obtained. The colour of the green film is doubtless to be ascribed to the same causes which operate in the case of gold leaf. The tint of the blue and purple films, however, is changed by moistening the plate with ligroin, precisely as is the case with potassium deposits. The mere approach of a glass rod, moistened with the liquid, is sufficient to produce a change of colour, the film apparently possessing the power of condensing the vapour upon its surface. Platinum and other metals in a fine state of division have this same property, consequently it seems extremely probable that the gold deposit is of this nature. Thus far I have only obtained two or three deposits which show this change. Most of the films are but slightly, if at all, affected by ligroin.

In the case of the gold films, the particles are too small to be seen under the microscope, with the facilities at my disposal; and I am inclined to the opinion that, in the case of the sodium and potassium films, particles which were actually seen with the microscope were only the moderately large ones, and may not have been instrumental in producing the colour. In continuing the work, I plan to make more exhaustive examinations with the microscope, using higher powers if possible, employing photography, and ultra-violet

light if necessary, for I believe that only in this way can the nature of the resonator be determined. There will be no great difficulty in determining the dispersion, since the gold films are permanent, and can be examined with the interferometer, or they may easily be given a prismatic form. I feel confident that they will show anomalous dispersion, a phenomenon which, if observed, would be almost proof positive that the absorption-band was due to resonance. It would not, however, enable us to decide whether the resonance was within the molecule or not, for prisms built up of tinfoil strips were found by Garbasso and Aschkinass\* to refract and disperse electromagnetic waves. Rubens and Nichols have examined the action on heat-waves of resonator systems formed by ruling crossed gratings on thin silver films, and found evidences of a higher reflexion percentage when the length of the resonators approaches a whole number of half wave-lengths.

Prof. Nichols and I are, at the present time, working in collaboration on the selective reflexion from a number of plates covered with resonators, very much smaller than any that have hitherto been employed. By depositing thin films of gold *in vacuo*, on glass, and ruling under oil, I have succeeded in producing resonators measuring  $0.8\mu$  by  $1.1\mu$ , which should resonate in a part of the spectrum where there is plenty of energy. Some of the trial rulings were made on the blue and purple films which I have mentioned, and in examining them under the microscope I have detected numerous minute granules, of about the same size as the sodium particles which I described in my previous paper. Whether these are the particles deposited by the cathode discharge, or merely metallic dust cut off by the diamond point, I am unable to say. The fact that the coloured films of gold are produced when the glass plate is at some distance from the cathode, seems to indicate that the gold vapour, if we may use the term, has time to condense into minute drops before reaching the plate. These films adhere much less firmly to glass than the green films which are formed when the distance between the cathode and the plate is small. In the

\* Wiedemann's *Annalen*, vol. liii. p. 534.

latter the deposit is doubtless molecular, and the optical properties are similar to those of gold leaf. I have thus far been unable to obtain coloured deposits of platinum, which is the only other metal I have examined at the present time, which fact makes it seem as if the molecule was in some way concerned with the colour. The variable nature of the colour, however, especially in the case of sodium and potassium, makes it appear improbable that the action is similar to that of aniline dyes; namely, a resonance within the molecule; for deposits of the same substance can be obtained showing an absorption-band almost anywhere in the visible spectrum, which is not the case with the more common types of coloured media.

The colour of the gold deposit varies, as I have said, with the conditions under which the deposition takes place. I have employed gold cathodes of two forms: a flat plate about 3 cms. square, and a thick wire, screening off the radiation from all but the tip with a mica screen. The most interesting deposits were obtained from the small source. In one instance the film showed a brilliant green surface colour, resembling fuchsine, the transmitted light having a purple tint. Owing to the transparency of the film a good deal of white light is mixed with the selectively reflected light; this can be cut off with a nicol, if the reflexion takes place at the polarizing angle for glass, and the coloured light from the film which is unpolarized then appears in great purity. One plate showed patches of brilliant carmine red, deep blue, and green, of an intensity and saturation which I have never seen equalled in any interference experiment. The colour of the selectively reflected light depended somewhat on the angle of incidence, a phenomenon observed also in the case of the sodium and potassium films. Increasing the angle of incidence changed the colour from green to blue; the period of vibration of the resonator system appears therefore to be less when the angle of incidence is large.

If the glass plate is placed near the tip of the gold wire, the green deposit, similar to gold leaf in its optical properties, is deposited at the centre. Surrounding this is a film appearing light yellow by transmitted light, and bluish by reflected light. This seems to be what we should expect, for the

smallest particles, which will resonate for blue light, will be deposited when the distance from the cathode is a little greater than that at which the molecular deposit occurs. Increasing the distance, we get larger particles, and the point of maximum resonance moves up into the green, giving us a purple film with green surface colour. At a still greater distance we get particles large enough to resonate for red, and the film appears deep blue by transmitted light. All of these variously coloured films can be changed into the green structureless film by heating. We may regard the change as due to the fusing together of the resonators. If this is the case, the electrical resistance should be less after firing than before. This was found to be the case. The conductivity of the films is surprisingly good. A strip of a deep blue film measuring 10 by 5 mms. had a resistance of only a little over 2 ohms. After heating the film its resistance dropped to about half this value.

It is even possible to change the colours by heating without sending the film over to the gold-leaf stage. I have a yellow film which local heating has changed to blue and purple in spots. A similar temperature change was noticed with the sodium and potassium films, as I mentioned in my previous paper, which I was unable to explain satisfactorily, since it appeared to be the opposite to what we should expect, if it was due to evaporation, which was the only thing that occurred to me at the time. It now seems as if the changes in both instances could be referred to a partial coalescing of the resonators.

I find a difficulty in reconciling the assumed resonance of the films with their electrical conductivity, but the matter is perhaps less troublesome than the explanation of why gold-leaf transmits any light at all.

Coloured films of a similar nature can be made of silver, by pouring a solution of Carey Lea's soluble allotropic silver on a glass plate and evaporating it over a flame\*. Ten parts of the ferrous sulphate solution are mixed with fourteen parts of the sodic citrate solution, to which is then added ten parts

\* American Journal of Science, vol. xxxvii. p. 476 (1889).

of the silver nitrate. The precipitate is allowed to settle, the liquid decanted, and the residue filtered. A small amount of distilled water is next poured into the filter and allowed to run through. More distilled water is now passed through the filter and collected. It will be found to have a very deep red colour, and if a small amount be spread over a clean glass plate and evaporated, it leaves a film which appears deep red, purple, and blue by transmitted light. The reflected light is of a complementary tint, the purple film reflecting green, and the green a greenish blue.

Ligroin changes the optical properties of the film, though the change is only to be seen when a nicol is used, and even then it is not very pronounced. I feel pretty certain that I have detected traces of a granular structure in these silver films with the microscope, and hope to confirm the observations as soon as a more perfect objective is at my disposal.

An investigation of the dispersal of the films, which I intend to take up next, and a more careful study with polarized light, will doubtless throw further light on the matter.

Baltimore, Md., U.S.A.,  
May 30, 1902.

XXVII. *On the Thermodynamical Correction of the Gas-Thermometer.* By H. L. CALLENDAR, M.A., F.R.S.,  
*Professor of Physics, Royal College of Science* \*.

1. *Introduction.*

THE correction of the gas-thermometer to the absolute scale is a subject possessing considerable theoretical interest ; it has also acquired some practical importance at the present time in view of the increasing accuracy attainable in thermometric measurements. A number of papers on the subject have recently appeared in the *Philosophical Magazine* and other periodicals. These show some divergence in the methods proposed and in the results deduced, and little has yet been done in the direction of calculating tables of corrections for different gases, or in the practical application of the results to thermometric measurements.

I propose in the present paper to give some account of the theoretical and experimental work bearing on the subject ; to explain a method of expression in terms of the "Co-aggregation Volume" which I have found very convenient in treating similar problems relating to imperfect gases ; and to show how to calculate tables of corrections in a simple and practical manner.

The earliest work of any value was that of Regnault (*Mémoires de l'Institut*, Paris, 1847) (1) on the deviations of gases from Boyle's law ; (2) on the pressure- and expansion-coefficients at various pressures ; (3) on the comparison of the thermometric scales of different gases over the range  $0^{\circ}$  to  $300^{\circ}$  C. These experiments established the suitability of the gas-thermometer as a standard, but the order of accuracy attained in the comparisons did not suffice to detect any difference between the scales of the more permanent gases.

The Absolute or Thermodynamic scale of temperature was invented shortly afterwards by Lord Kelvin, who devised a

\* Read March 26th, 1901. Publication was delayed to await the results of experiments in progress at University College. But in consequence of my removal to the Royal College of Science, it has been found impossible to include this experimental work in the present paper.



very delicate method of detecting the deviations of actual gases from the ideal state (Trans. Roy. Soc. Edinb. vol. xx. p. 289, April 1851; Phil. Mag. [4] 1852, p. 481), and explained how to reduce the indications of the gas-thermometer to the absolute scale. The experimental measurements were carried out shortly afterwards in conjunction with Joule (Phil. Trans. 1854, p. 321), and still remain among the most important data for the determination of the thermodynamical correction. The history of this investigation is contained in Sir Wm. Thomson's Mathematical and Physical Papers, vol. i. pp. 333-455, and need not be considered in detail; but it will be necessary to give a brief account of the method for the elucidation of the notation adopted and the method of calculation proposed in the present paper.

## 2. *Theory of the Porous-Plug Experiment* \*.

The notation adopted is as follows :—

$E$  = intrinsic energy of fluid per unit mass.

$p$  = pressure;  $v$  = volume of unit mass.

$F = E + pv$  = total heat of fluid per unit mass.

$H$  = heat supplied per unit mass from external sources.

$Q = (d\theta/dp)_F$  = "Cooling Effect," or fall of temperature per unit fall of pressure in adiathermal expansion at constant  $F$ .

$S = (dH/d\theta)_p$  = specific heat of fluid at constant pressure.

$T = (pv/R)$  = temperature by gas-thermometer.

$\theta$  = temperature on the thermodynamic scale.

We have the following relations between the different quantities :—

By the first law of thermodynamics,

$$dE = dH - pdv. \quad . \quad . \quad . \quad . \quad . \quad (1)$$

By the second law of thermodynamics,

$$(dH/dp)_\theta = -\theta(dv/d\theta)_p. \quad . \quad . \quad . \quad . \quad (2)$$

Whence,

$$\begin{aligned} dF &= dE + d(pv) = dH + vdp \\ &= (dH/d\theta)_p d\theta + (dH/dp)_\theta dp + vdp \\ &= Sd\theta - (\theta(dv/d\theta)_p - v)dp. \quad . \quad . \quad . \quad (3) \end{aligned}$$

\* For practical details see Preston, 'Theory of Heat,' p. 702 (1894); Edser, 'Heat for Advanced Students,' p. 384.

When a fluid is flowing steadily along a tube through a porous plug or throttling aperture without external loss or gain of heat, as in the experiment of Joule and Thomson, the function,  $F = E + pv$ , will remain constant provided that the kinetic energy of flow is the same on either side of the plug. It is convenient to have a name for this function, which I have called the Total Heat, employing the expression used by Regnault for the same quantity in the case of a saturated vapour. Expansion through a porous plug is frequently spoken of as "free" or "unresisted" expansion, but this term appears to be inappropriate, since the external work done is  $d(pv)$  and not zero, as in Joule's original experiment. It is often said to be "adiabatic" in the sense that no heat is supplied to the fluid from external sources. But this may lead to some confusion, as the process is not isentropic. I have found the term "Adiathermal" more convenient, as implying that there is no heat-transmission, and that the total heat remains constant ( $dF = 0$ ).

Applying the condition  $dF = 0$ , we have by (3) above the well known relation,

$$SQ = S(d\theta/dp)_F = \theta(dv/d\theta)_p - v. \quad \dots (4)$$

This equation gives the "cooling effect" in adiathermal expansion under the condition of constant total heat, which is the quantity measured in the porous-plug experiment. It is convenient to employ the single letter  $Q$  for the cooling effect  $(d\theta/dp)_F$ , and to measure it in degrees of temperature centigrade per atmosphere ( $p = 10^6$  c.g.s. = 75 cms. Hg. at  $0^\circ$  C. and lat.  $45^\circ$ ), in which case  $S$  should also be measured in terms of a unit  $10^6$  ergs. The sign of  $Q$  is positive when a fall of temperature accompanies a fall of pressure, as in the case of air and  $\text{CO}_2$ . It is negative, a heating effect, in the case of hydrogen at ordinary temperatures.

It is important to observe that the vanishing of the cooling effect is not in itself a sufficient criterion of the ideal gaseous state,  $pv = R\theta$ . The condition  $\theta(dv/d\theta)_p = v$  would evidently be satisfied by any fluid possessing the characteristic equation  $v/\theta = f(p)$ , where  $f(p)$  is any arbitrary function of  $p$ . But if the fluid satisfies Boyle's law at all temperatures, we must have  $pv = f(\theta)$ , and the two conditions together are satisfied

only by the ideal gas. Similarly Joule's experiment on the expansion of a gas into a vacuum ( $dE=0$ ) leads to the condition  $\theta(dp/d\theta)_v=p$ , if there is no change of temperature, which is satisfied by any fluid possessing the characteristic equation  $p/\theta=f(v)$ , where  $f(v)$  is any arbitrary function of  $v$ . This condition, in conjunction with Boyle's law, again suffices to define the ideal state; but no one of the three conditions is sufficient by itself.

### 3. Application to the Gas-Thermometer.

In the practical application of the gas-thermometer, we assume an equation of the form  $pv=RT$ , in which  $T$  is the temperature by gas-thermometer; and differs from  $\theta$  in proportion as the gas in question deviates from the ideal state. In order to apply the results of the porous-plug experiment to the correction of the scale of the gas-thermometer, Thomson originally proposed to estimate the difference  $\theta-T$  approximately by the following method:—

Suppose the experiment to be performed in a calorimeter at constant temperature, so that the gas after passing the plug is restored to its initial temperature. The heat absorbed in the calorimeter is evidently equal to the amount  $Sd\theta$  which would have been required to heat the gas up to the original temperature at constant pressure if the experiment had been performed adiathermally with a fall of temperature  $d\theta$ . But the heat absorbed at constant temperature in the calorimeter is also by the first law equal to the increase of intrinsic energy  $(dE/dv)_\theta dv$  of the gas, together with the external work  $d(pv)_\theta$  done by the gas. Writing for  $(dE/dv)_\theta$  its value  $\theta(dp/d\theta)_v-p$ , we have

$$-Sd\theta = (\theta(dp/d\theta)_v - p)dv + d(pv), \quad \dots (5)$$

which is evidently equivalent to the equation (4) previously given, but with  $v$  instead of  $p$  as independent variable, since  $(dp/d\theta)_v(dv/dp)_\theta = -(dv/d\theta)_p$ . Integrating this expression over the range of an experiment from  $p'v'$  to  $p''v''$  at constant temperature, and putting on the left the observed value of the fall of temperature  $(\theta' - \theta'')$ , we obtain Thomson's original equation,

$$S(\theta' - \theta'') = \theta(dW/d\theta)_v - W + p''v'' - p'v', \quad \dots (6)$$

in which  $W$  is the work represented by the integral of  $p dv$  at constant temperature. The integral  $W$  and its variation with temperature cannot be determined for the gas without an exact knowledge of the form of the isothermals, and of the coefficient  $(dp/d\theta)_v$  in terms of the absolute scale. Thomson therefore proposed to make an approximate estimate by assuming (1) that the gas obeyed Boyle's law  $p'\theta' = RT = p''\theta''$ , (2) that the degrees on the absolute scale were nearly the same size as on the constant-volume gas-thermometer at the temperature of experiment, or that we may write  $(dp/d\theta)_v = (dp/dT)_v = p/T = R/v$ . Making this approximation, we obtain immediately,

$$\theta - T = S(\theta' - \theta'')/R \log_e (\theta''/\theta'). \quad (7)$$

This approximation is unsatisfactory, because if we knew the absolute value of the pressure-coefficient and the deviations from Boyle's law, the gas-thermometer might be corrected to the absolute scale without performing the porous-plug experiment. The quantities neglected are evidently of the same order as the quantity sought. Thomson and Joule clearly realized this, and devised other methods of correction, but unfortunately the first approximate solution is still retained in many text-books\*, in a slightly different form, as the final and correct solution of the problem. The method of exposition generally adopted is as follows:—

Assuming that the degrees on the scale of the constant-pressure gas-thermometer are of the same size as those of the absolute scale at the temperature of the experiment, we may write  $dv/d\theta = dv/dT = R/p$  in equation (4). Rearranging the terms and substituting  $T$  for  $p v/R$ , we then obtain

$$\theta - T = S p d\theta / R d p. \quad (8)$$

Assuming further that the small difference  $(\theta - T)$  is independent of  $p$ , the right-hand side is integrated from  $p'$  to  $p''$ , substituting for  $d\theta$  the actual difference of temperature  $(\theta' - \theta'')$  observed when the gas expands adiathermally from a pressure  $p'$  to a pressure  $p''$ . This gives again the expression

$$\theta - T = S(\theta' - \theta'')/R \log p'/p'' = S(\theta' - \theta'')/R \log \theta''/\theta'. \quad (9)$$

\* *E. g.* Maxwell's 'Heat,' p. 214 (1897); Tait's 'Heat,' p. 340 (1895).

When the experiment was tried, it was found that the fall of temperature ( $\theta - \theta'$ ) was *not* proportional to  $\log(p/p')$ , but simply to  $(p - p')$ , so that the second assumption involved in solution (9) is evidently erroneous. As a matter of fact, Joule and Thomson did not make any direct use of the approximate solution in this form. But owing to its frequent repetition, it has proved a stumbling-block to many who have attempted to apply the results of these experiments to the calculation of the difference between the scales.

In order to calculate the correction for the *air*-thermometer over the whole range, Joule and Thomson proceeded in 1854 by a different method. Combining Regnault's formula for the pressure-coefficient at various constant densities, namely,

$$\text{Pressure-coefficient of Air} = \cdot 00365343 + \cdot 000011575 V_0/v, \quad (10)$$

with his experiments on the deviations from Boyle's law at  $4^\circ \text{C.}$ , and with their own experiments on the cooling-effect, they calculated the following formula (the units being feet and pounds) to satisfy all the available experimental data:—

$$pv = R(\theta - (\cdot 0012811 - 1\cdot 3918/\theta + 353\cdot 2/\theta^2)V_0/v). \quad (11)$$

This is a very simple and direct method provided that the data employed are accurate and consistent. Calculating from this formula they obtained the value of the freezing-point of water on the absolute scale  $0^\circ \text{C.} = 273\cdot 72 \text{ Abs.}$ , which is still frequently quoted, and was universally accepted for many years. They also calculated a table of corrections for the air-thermometer which has been quoted in many recent books (*e. g.* Guillaume's *Thermométrie*, Paris, 1889) as the final result of their work. It is evident, however, that the value  $0^\circ \text{C.} = 273\cdot 72 \text{ Abs.}$  is simply the reciprocal of Regnault's limiting coefficient at zero initial pressure, namely,  $\cdot 00365343$ , and does not depend at all on the value of the cooling-effect; and since Regnault's formula (7) is well known at the present time to be erroneous, it is not to be wondered at that the values of the thermodynamical correction given in Joule and Thomson's original table should be very greatly in excess of the true difference between the scales.

Other attempts have been made on similar lines to calculate

tables of reduction for the gas-thermometer, notably by Jochmann (1860), and by Weinstein (1881), whose results are quoted in Guillaume's *Thermométrie*, p. 261 \*. Weinstein quotes Jochmann's equation, and endeavours to adapt the method for calculation of the corrections of the constant-volume thermometer. By a somewhat complicated method, taking account of Regnault's data in addition to those of Joule and Thomson, he arrives at an empirical equation of the form

$$\theta/\theta_0 = (1 + 0.003654 t)^{1.00029}, \quad . . . \quad (12)$$

in which  $t$  is the temperature on the centigrade scale. The values of the corrections calculated by this method are much smaller than those in the original table of Joule and Thomson, and are of the right order of magnitude between  $0^\circ$  and  $100^\circ$ , but it does not appear that an equation of this type correctly represents the phenomena.

#### 4. Rankine's Equation for $\text{CO}_2$ .

In the same paper (Phil. Trans. 1854, p. 337) Joule and Thomson quoted another empirical formula for  $\text{CO}_2$ , contained in a letter from Rankine, namely,

$$pv = R\theta - aR\theta_0 v_0/\theta v, \quad . . . \quad (13)$$

in which the value of the constant  $a$  (in degrees of temperature) was given as 1.9, and was deduced solely from Regnault's observations of the pressure-coefficient of  $\text{CO}_2$  at various constant densities. In a previous paper (Trans. Roy. Soc. Edinb. xx. p. 561) Rankine had given an estimate of  $\theta_0$ , the absolute zero, obtained by plotting Regnault's values of the pressure-coefficients of air and  $\text{CO}_2$ , which led to the value  $\theta_0 = 274^\circ.6$ , but in the formula quoted he employed  $\theta_0 = 274^\circ.0$ . This formula agreed very well with Regnault's coefficients of expansion for  $\text{CO}_2$ , and also with his observations on the compressibility. Joule and Thomson further showed that it satisfied their own observations on the cooling-effect at that time available, employing the expression  $Q = 3Ra\theta_0^2/S\theta^2$ , deduced from Rankine's formula. Taking Rankine's value for  $a$ , and putting  $R = 1.89 \times 10^6$ ,  $S = 8.4 \times 10^6$

\* Jochmann, *Schlomilchs' Zeit. Math. Phys.* v. pp. 24 & 96; Weinstein, *Metron. Beitr.* n. 3, p. 65.

c.g.s. we find  $Q$  at  $0^\circ \text{C.} = 1^\circ.28$  per atmo., which is in fair agreement with the value actually observed.

At a later date (Phil. Trans. 1862) Joule and Thomson succeeded in obtaining more accurate measurements of the cooling-effect over a range of temperature extending from  $4^\circ$  to  $96^\circ \text{C.}$ , and found that the cooling-effect for air and  $\text{CO}_2$ , varied nearly as  $1/\theta^2$ , and could therefore be represented by Rankine's formula. By adopting the expression  $Q = A/\theta^2$  for the cooling-effect, and integrating equation (4), neglecting the variations of  $S$ , and assuming that the equation must approximate indefinitely to  $v = R\theta/p$  at high temperatures, they obtained the following type of characteristic equation,

$$v = R\theta/p - AS/3\theta^2, \quad . \quad . \quad . \quad (14)$$

which may also be obtained by substituting  $pv = R\theta$  in the small term of Rankine's. They found, however, that the heating-effect in the case of hydrogen increased slightly with rise of temperature, and could not be represented by the formula. Assuming Rankine's formula, it would evidently be easy to calculate the value of the absolute zero, and to deduce tables of corrections for the gas-thermometer. But as the formula did not represent the case of hydrogen, which was the most important for thermometric purposes, they did not publish any further tables of corrections, and the absolute zero was still taken at  $-273^\circ.7 \text{C.}$ , as calculated in their previous paper from Regnault's limiting value for the pressure-coefficient in the case of air.

##### 5. *Estimation of the Absolute Zero.*

The problem of the thermodynamical correction of the gas-thermometer is naturally divided into two parts: (1) the determination of the value of the freezing-point of water on the absolute scale in terms of the fundamental interval, which may be called the value of the Absolute Zero; (2) the determination of the correction to be applied at other points of the scale to reduce an interval of temperature measured on the scale of the gas-thermometer to the corresponding value measured on the absolute scale, which may be called the Scale-Correction. The latter depends essentially on the type of empirical formula assumed to represent the mode of

variation of  $Q$  with temperature, whereas the former may be approximately estimated without any such assumptions. Moreover, the scale-correction is necessarily small for gases at ordinary temperatures, whereas the absolute zero correction may be considerable, and is required for determining the variations of the pressure- and expansion-coefficients.

A simple and accurate method of determining the value of the absolute zero from observations of the cooling-effect alone, was given by Sir Wm. Thomson in his article "Heat" in the *Encyclopædia Britannica* (vol. xi. p. 554, 1880). The differential equation (4) may be written in the form

$$d\theta/\theta = dv/(v + SQ), \quad . . . . (15)$$

in which, if we require only to make an approximate estimate of the absolute zero correction, we may put  $SQ$  constant and equal to its average value between  $0^\circ$  and  $100^\circ$  C. Integrating this at constant pressure  $p_0$  between limits  $0^\circ$  and  $100^\circ$ , and writing  $T_0$  for the expression  $100v_0/(v_{100} - v_0)$  (the reciprocal of the fundamental coefficient of expansion, which may be called the "fundamental zero"), we obtain for the absolute zero correction the simple result,

$$\theta_0 - T_0 = Sp_0Q/R. \quad . . . . (16)$$

This expression was applied to calculate the coefficients of expansion at various constant pressures, and to determine the value of the absolute zero from Regnault's coefficients of expansion of air, hydrogen, and  $\text{CO}_2$  at  $p_0 = 76$  cms.

The following table contains the results given in the article in question :—

TABLE I.—Absolute Zero from Regnault's  
Expansion-Coefficients.

Gas employed .....	Air.	$\text{H}_2$ .	$\text{CO}_2$ .
Coefficient of Expansion, $\alpha$ .....	0036706	0036613	0037100
Fundamental Zero of Gas, $T_0 = 1/\alpha$ ...	272° 44	273° 13	269° 50
Correction to Absolute Zero, $\theta_0 - T_0$ ...	+70	-13	+44
Absolute Zero deduced, $\theta_0$ .....	273 14	273 00	273 90

Thomson remarks as the result of these figures that the correct value is probably within a tenth of a degree of  $273^\circ 0$ , and that it is satisfactory to find that a gas so imperfect as



CO<sub>2</sub>, with so large a value of the correction, should differ so little when corrected from air and hydrogen. As a matter of fact, the discrepancy, small as it is, appears to be due to an error in Regnault's coefficient of expansion, for if we adopt instead Chappuis' value of the expansion-coefficient for CO<sub>2</sub> at 100 cms. pressure, namely .003742, which gives  $T_0 = 267^\circ.24$ , we find (increasing the correction in the ratio 100/76) the value of the absolute zero  $\theta_0 = 267^\circ.24 + 5^\circ.8 = 273^\circ.04$ , which agrees with hydrogen.

A similar method has been applied by other writers to estimate the zero correction for the constant-volume thermometer. If we neglect the term  $d(pv)$  in equation (5) (which is *not* justifiable), and write  $-(d\theta/dv)_p = Qp/v$  (which is a good approximation considering that this term is small), we obtain

$$1 + SQ/v = (dp/d\theta)_p \theta/p. \quad (17)$$

Integrating this at constant volume, *assuming SQ constant*, we have the solution

$$\log_e (\theta/\theta_0) = \log_e (p/p_0)/(1 + SQ/v), \quad (18)$$

from which, since SQ is small, we have the approximate value of the correction,

$$\theta_0 - T_0 = 1.163 Sp_0 Q/R. \quad (19)$$

This is equivalent in effect to the method adopted by Lehfelddt (Phil. Mag. April 1898, p. 363), who takes for Q the value of the "proper mean cooling-effect" given by Thomson. Applying the correction to the value of the pressure-coefficient for CO<sub>2</sub> found by Chappuis at  $p_0 = 100$  cms., namely, .0037251,  $T_0 = 268^\circ.45$ , he finds  $\theta_0 = 274^\circ.83$ , which is evidently much too large. The error is chiefly due to the neglect of the term  $d(pv)$ . He also applies formula (18) to evaluate the scale-correction between 0° and 100° for comparison with Chappuis' observations. His results for the scale-difference between the nitrogen and hydrogen thermometers are given in Table VI. (p. 303), and indicated by the dotted curve in fig. 1 (p. 305). They appear to be somewhat in excess of the true values, partly in consequence of the assumption  $SQ = \text{constant}$ , which cannot be made in deducing the scale-correction.

There is a much simpler method of deducing the absolute zero correction directly from the differential equation, without integrating on the assumption  $SQ = \text{constant}$ , which, so far as I am aware, has not been previously noticed.

For the constant-pressure thermometer, we take the equation in the form (4), and substitute  $dv/d\theta = R/p$ , and  $T = pv/R$ , which gives the simple result,

$$\theta - T = SpQ/R, \quad . . . . . (20)$$

which is accurately true at a point in the neighbourhood of  $50^\circ \text{C.}$ , where the degrees on the scale of the gas-thermometer are of the same size as those on the absolute scale. To find the value of the zero correction  $\theta_0 - T_0$ , we have merely to subtract the value of the scale-correction at this point. But the latter must be very small compared with the zero correction, since the whole number of degrees between  $0^\circ$  and  $100^\circ \text{C.}$  is the same by definition for both thermometers. If, therefore, we substitute the proper mean value of  $SQ$ , which corresponds to the point where the degrees are of equal size, we shall obtain a very good approximation to the absolute zero correction, which is in fact seen to be the same as that given by Thomson for the constant-pressure thermometer.

To make a similar estimate for the constant-volume thermometer, we take the differential equation in the form (5), which may be written

$$-SQ(dp/dv)_F = \theta(dp/d\theta)_\theta - p + (d(pv)/dp)(dp/dv)_\theta. \quad (21)$$

In the small terms it is justifiable to make the approximations  $(dp/dv)_F = (dp/dv)_\theta = -p/v$ . If we also put  $(dp/d\theta)_\theta = R/v$ , which is only true at the point where  $dT/d\theta = 1$ , we obtain

$$\theta - T = SpQ/R + (d(pv)/dp)_\theta p/R. \quad . . . (22)$$

In order to evaluate this for  $\text{CO}_2$  we may take  $SQ = 7.9 \text{ c.c.}$  as the proper mean value. We require in addition the value of  $d(pv)/dp$  at or near  $50^\circ \text{C.}$ , which may be taken as  $2.4 \text{ c.c.}$  from Amagat's observations on  $\text{CO}_2$ . The value of  $p$  is the pressure in the gas-thermometer at the point considered. Adopting Chappuis' value of the pressure-coefficient for  $\text{CO}_2$  at 100 cms. initial pressure, namely,  $.0037251$ ,  $T_0 = 268^\circ.45$ , we have  $p = 119 \text{ cms.} = 1.58 \times 10^6 \text{ c.g.s. at } 50^\circ$ . Taking

$R=1.89 \times 10^6$ , we find the value of the correction  $4^{\circ}.55$ , which gives  $\theta_0=273^{\circ}.0$ . This neglects the scale-correction at  $50^{\circ}$ , which, however, is less than  $.05^{\circ}$ . It is clear that the correction depending on  $d(pv)$  cannot be neglected. If we could replace  $Q$  by the cooling-effect in "free" expansion ( $dE=0$ ), as in Joule's original experiment, this term would not be required.

#### 6. *The Equations of van der Waals and Clausius.*

The above method of deducing the value of the absolute zero from the cooling-effect may appear at first sight to be wanting in precision; but it assumes only that the effect is small, and diminishes continuously with increase of temperature, and the results to which it leads are really quite as accurate as the available experimental data. By way of contrast we may take a method which appears at first sight to be unimpeachable, but which leads to results which are obviously wrong.

Van der Waals, in his celebrated essay "On the Continuity of State" (Phys. Soc. Translation, Cap. XI. p. 440), was the first to interpret the cooling-effect in terms of the capillary pressure represented by the term  $a/v^2$  in his well known equation

$$(p + a/v^2)(v - b) = R\theta. \quad . \quad . \quad . \quad (23)$$

Taking this equation, he showed that, if the capillary pressure varied inversely as the square of the volume, and the co-volume  $b$  was constant, the fall of temperature in the Joule-Thomson experiment must be to a first approximation proportional to the fall of pressure, or the ratio  $Q$  independent of  $p$ . The expression which he gave for the cooling effect is equivalent to the following:

$$SQ = 2a/R\theta - b. \quad . \quad . \quad . \quad (24)$$

As applied to the constant-volume thermometer, the equation gives very simple results, since  $p$  is accurately a linear function of  $\theta$ , so that the scale-correction is identically zero. The absolute zero correction is given by the formula

$$\theta_0 - T_0 = a/Rv = ap_0/R^2\theta_0. \quad . \quad . \quad . \quad (25)$$

Van der Waals himself observed that the values of  $a$  and  $b$  which he adopted for  $\text{CO}_2$  to represent the experiments of

Regnault and Andrews did not satisfy the results of Joule and Thomson on the cooling-effect. Rose-Innes, however, has shown (Phil. Mag. March 1898, p. 227) that a formula of the type  $Q = A/T - B$  (which is the same as that given by van der Waals) represents the cooling-effect much better than that of Rankine, including the case of hydrogen, and has calculated the appropriate values of the constants. Adopting his values of the coefficients  $A$  and  $B$ , and taking  $S = 8.4 \times 10^6$ , we find for  $\text{CO}_2$

$$a/R\theta_0 = 11.9 \text{ c.c.}, \quad b = 12.3 \text{ c.c.} \quad . \quad . \quad (26)$$

Rose-Innes applied this formula to calculate the absolute zero from Regnault's expansion-coefficients, and obtained results practically identical with Lord Kelvin's; but he did not apply it to calculate the absolute zero from the pressure-coefficient. If we take, as before, Chappuis' pressure-coefficient for  $\text{CO}_2$  at  $p_0 = 100$  cms., namely,  $.003725$ ,  $T_0 = 268^\circ.45$ , the correction is  $8^\circ.4$ , which gives  $\theta_0 = 276^\circ.9$ , a result which is obviously much too large.

This discrepancy is partly due to the fact that the type of formula assumed to represent the variation of  $Q$  with temperature is wrong, although it represents the observations perfectly over the experimental range. It shows very clearly that the method previously given, which does not assume any particular type of formula, but deduces the zero correction directly from the observations, is much to be preferred, although it may appear less rigorous at first sight. Moreover, it is evident that the values of  $a$  and  $b$  deduced from the cooling-effect in this manner would not satisfy the observations of Regnault or Amagat on the isothermal compressibility, since they would make  $d(pv)/dp$  at  $0^\circ \text{ C.}$  (which is approximately given by the expression  $-(a/R\theta_0 - b)$ ) positive and equal to about  $+0.4$  c.c., *i. e.* the gas would appear "pluperfect," like hydrogen, whereas it is very much the reverse. If on the other hand we take the values of the constants given by van der Waals, which would be equivalent to the following,

$$a/R\theta_0 = 4.42 \text{ c.c.}, \quad b = 1.16 \text{ c.c.}, \quad . \quad . \quad (27)$$

the compressibility at  $0^\circ \text{ C.}$  is well represented, but the value of the cooling-effect is much too small. At higher tem-

peratures the formula gives values of the cooling-effect which are more nearly correct, but the value of  $d(pv)/dp$  at  $200^{\circ}\text{C}$ . is found to be  $-1.40$  c.c., which is nearly twice as large as the value given by Amagat's observations. The formula would also make the scale-correction of the constant-volume thermometer vanish at all temperatures, whereas the observations of Chappuis (see below) prove that it is quite large in the case of  $\text{CO}_2$ .

On these and similar grounds we are justified in concluding that the formula of van der Waals does not represent the behaviour of  $\text{CO}_2$  at moderate pressures with sufficient accuracy to be of practical value. Clausius, however, has shown (Phil. Mag. June 1880) that the agreement is greatly improved if we suppose the coefficient  $a$  in the capillary pressure to vary inversely as  $\theta$ , which leads to a formula of the same type as that proposed by Rankine, but with the addition of the covolume  $b$ . For the purposes of gas-thermometry, or for calculations at moderate pressures, we may neglect quantities of the second order, and may write the equation of Clausius in the form

$$v = R\theta/p - a/R\theta^2 + b. \quad . \quad . \quad . \quad (28)$$

Love (Phil. Mag. July 1899) has shown that a formula of this type represents all the observations on the cooling-effect very well, but he has not applied it to the calculation of the absolute zero, or the scale-correction of the gas-thermometer.

### 7. *Expression in Terms of the Co-aggregation-Volume c.*

In the application of this or similar equations to represent the behaviour of imperfect gases at moderate pressures, I have found it very convenient to employ the single letter  $c$  to represent the term  $a/R\theta^2$ . The quantity  $c$  represents a volume, expressible in cubic centimetres, which is to a first approximation a function of the temperature only, and which may be called the "co-aggregation-volume," as it denotes the diminution of volume caused by the formation of molecular aggregates. All the thermodynamical properties of the gas may be simply expressed (as I have shown, Proc. Roy. Soc. 1900, vol. lxvii. p. 266) in terms of the co-aggregation-volume. This method of expression is more convenient for

practical purposes than expression in terms of the capillary pressure, since the latter is a function of both volume and temperature. It is convenient to assume that  $c$  varies inversely as the  $n$ th power of  $\theta$ , so that we may write

$$c = c_0(\theta_0/\theta)^n, \quad \dots \dots \dots (29)$$

where  $c_0$  is the value of  $c$  at  $\theta_0$ . The value of the index  $n$  is apparently 2 for  $\text{CO}_2$ , but it may have different values for other types of molecules. The general expression for the cooling-effect deduced from (4) on this assumption is

$$\text{SQ} = (n+1)c - b, \quad \dots \dots \dots (30)$$

and the expression for the slope of the isothermals obtained by plotting the product  $pv$  against  $p$  is

$$d(pv)/dp = -(c-b). \quad \dots \dots \dots (31)$$

For an imperfect gas like  $\text{CO}_2$  or nitrogen,  $c$  is greater than  $b$ . The gas becomes "pluperfect," like hydrogen, at the point where  $c=b$ . The isothermals on the  $pv, p$  diagram are straight lines, the inclinations of which to the axis of  $p$  diminish as the temperature rises. This is a much better approximation than might be supposed at first sight, because experiment shows the isothermals to be nearly straight for a considerable range of pressure and temperature.

If we calculate the values of the constants  $c_0$  and  $b$  for each gas from the experiments of Joule and Thomson on the cooling-effect, employing the equation (28) above with the value  $n=2$ , so that  $\text{SQ}=3c-b$ , we obtain the results given in the following table :—

TABLE II.—Values of Constants from Observations of Joule and Thomson.

Gas employed.	R. × 10 <sup>4</sup> .	S. × 10 <sup>4</sup> .	Q <sub>0</sub> .	Q <sub>100</sub> .	c <sub>0</sub> . c.c.	b. c.c.	C. c <sub>0</sub> p <sub>0</sub> /373R.
			Per atmo. (10 <sup>4</sup> c.g.s.)				
Air .....	2.871	10.05	0.271	0.147	0.90	— .002	.00085
CO <sub>2</sub> .....	1.887	8.40	1.368	0.610	4.56	2.18	.00656
H <sub>2</sub> .....	41.5	145.3	— .029	— .048	2.01	10.23	.000132

The constant  $C$  is employed in calculating the scale-corrections in Table VI. below. The values are given for  $p_0 = 76 \text{ cms.} = 1.0133 \times 10^6 \text{ c.g.s.}$

### 8. *Method of Calculating the Correction.*

An incomplete table of corrections, for the air-thermometer only, was calculated by Rowland (Proc. Amer. Acad. vol. vii. 1880, p. 114) with the object of correcting the air-thermometer which he employed in the reduction of his observations on the mechanical equivalent of heat. The method of calculation was not given, but he employed only Joule and Thomson's later results (1862) as represented by Rankine's equation. His work was probably the first application of the thermodynamical correction to the actual results of experiment.

A similarly incomplete table of corrections for the air-thermometer was given in my own paper "On the Practical Measurement of Temperature" (Phil. Trans. A. 1887, p. 162) for reducing the indications of the platinum-thermometer to the absolute scale. The method of calculation adopted was as follows.

For purposes of gas-thermometry the characteristic equation of the gas employed may be written in the following form :

$$\theta = pv/R + q, \quad . . . . . (32)$$

in which  $q$  is a small quantity of the dimensions of temperature, which represents the deviations of the gas from the ideal state. In using a gas-thermometer we assume an equation of the type  $T = pv/R'$ , in which  $T$  is the temperature on the scale of the gas-thermometer, and  $R'$  is a constant, differing slightly from  $R$ , and depending to some extent on the method of thermometry employed. The values of  $R$  and  $R'$  are determined in each case from the observations at the fixed points  $0^\circ$  and  $100^\circ \text{ C.}$ , which give the following relations :

$$R' = (p_1 v_1 - p_0 v_0)/100, \quad R = R'(1 + (q_1 - q_0)/100), \quad (33)$$

in which  $p_0, v_0, q_0$  are the values of  $p, v, q$  at  $0^\circ \text{ C.}$ , and  $p_1, v_1, q_1$  are the values at  $100^\circ \text{ C.}$  In deducing these

relations small quantities of the second order involving squares and products of  $q$  are neglected.

To find the value of the absolute zero we have the equation

$$\theta_0 = p_0 v_0 / R + q_0 = T_0 + q_0 - (q_1 - q_0) \theta_0 / 100. \quad (34)$$

To find the value of the correction  $dt$  to be added to the centigrade temperature  $t$  on the scale of the gas-thermometer to reduce to temperature centigrade on the thermodynamical scale, since the temperature centigrade on the scale of the gas-thermometer is given by the formula

$$t = T - T_0 = (pv - p_0 v_0) 100 / (p_1 v_1 - p_0 v_0), \quad (35)$$

we have evidently the simple expression

$$dt = (\theta - \theta_0) - (T - T_0) = (q - q_0) - (q_1 - q_0) t / 100. \quad (36)$$

It may be noticed with regard to the separate terms in this expression that  $q_0$  is the zero-correction, and the second part  $(q_1 - q_0) t / 100$  is the correction for the fundamental interval. The correction at any point of the scale is not simply  $q - q_0$ , as might appear at first sight, because the values of the constants  $R$  and  $R'$  are different, and the correction must vanish at  $100^\circ \text{C.}$  as well as at  $0^\circ \text{C.}$

In order to apply formula (36) to the calculation of a table of corrections, we may select any empirical formula which represents satisfactorily the properties of the gas under consideration. The equation is then thrown into the form (32), and the expression for  $q$  is simplified as far as possible by rejecting all quantities of the second order, and is expressed in terms of  $p_0$  and  $T$  or  $\theta$ . As a simple example we may take the equation devised by Clausius to represent the deviations of  $\text{CO}_2$  from the formula of van der Waals,

$$(p + a/\theta(v + \beta)^2)(v - b) = R\theta. \quad (37)$$

Neglecting small quantities of the second order, this may be put in the form

$$\theta = pv/R + (a/R\theta^2 - b)p/R, \quad (38)$$

whence

$$q = (a/R\theta^2 - b)p/R = (c - b)p/R. \quad (39)$$

Writing  $p_0$  for  $p$  we have the value of  $q$  for the constant-pressure thermometer. For the constant-volume thermometer we must substitute  $p_0 \theta / \theta_0$  for  $p$ . The values of the constants



may be immediately calculated (as above, Table II.) from the observations of Joule and Thomson on the cooling-effect, without reference to any other experimental data. A table of corrections calculated in this manner may not be the most accurate possible at the present time, when so many more observations are available, but it is of special interest to compare the results of an investigation made so long ago with those of the latest thermometric researches. For this reason I have calculated the following table of corrections on the basis of equation (38), assuming only the data already given for the cooling-effect according to Joule and Thomson.

In the simple case here considered it is unnecessary to calculate the values of  $q$  for each temperature separately, and then apply formula (36) to find the correction  $dt$ . The expression for  $dt$  may with advantage be greatly simplified, before beginning the calculation, by putting in the numerical values of  $\theta_0$  and  $\theta_1$ , namely, 273 and 373, and substituting  $t$  for  $\theta - \theta_0$ . We thus obtain the following simple formulæ.

For the Constant-Volume Thermometer:—

$$\text{Absolute Zero-Correction, } \theta_0 - T_0 = 646C, \quad . \quad (40)$$

$$\text{Scale-Correction, } dt = Ct(t-100)/\theta, \quad . \quad (41)$$

in which  $C$  is used as an abbreviation for the constant factor  $c_0 p_0 / 373R$ , which has the values given in Table II. above for an initial pressure  $p_0 = 760$  mm.

For the Constant-Pressure Thermometer:—

$$\text{Absolute Zero-Correction, } \theta_0 - T_0 = 846C - bp_0/R, \quad . \quad (42)$$

$$\text{Scale-Correction, } dt = Ct(t-100)(1.732 + 273/\theta)/\theta. \quad (43)$$

The covolume  $b$  occurs only in the zero-correction of the constant-pressure thermometer. The values of the constant  $C$  are the same as for the constant-volume thermometer. The corrections for the constant-pressure thermometer are deduced from those for the constant-volume thermometer by multiplying by the factor  $(1.732 + 273/\theta)$ , which has values between 2 and 3 at ordinary temperatures. When the corrections for any one gas have been calculated, those for any other follow by simple proportion. The corrections given in the table are all calculated for an initial pressure

$p_0 = 760$  mm. The corrections for any other initial pressure are simply proportional to the pressure.

If we apply the above formulæ to calculate the value of the absolute zero from Regnault's pressure-coefficients, we find considerable discrepancies in the results, as illustrated by the following table.

TABLE III.—Absolute Zero from Regnault's Pressure-Coefficients.

Gas employed .....	Air.	Hydrogen.	CO <sub>2</sub> .
Pressure-Coefficient ( $p=76$ cms.), $a$ ...	·0036650	·0036678	·0036880
Fundamental Zero of Gas, $T_0=1/a$ ...	272°·85	272°·64	271°·2
Correction to Absolute Zero, $\theta_0 - T_0$ ...	+ ·56°	+ ·09°	+4°·2
Absolute Zero deduced, $\theta_0$ .....	273°·41	272°·73	275°·4

It appears that these discrepancies are due in the main to errors of Regnault's pressure-coefficients, which subsequent observations have shown to be much less accurate than his expansion-coefficients, though Regnault himself considered them more accurate. If we employ Chappuis' values of the pressure-coefficients, which are certainly nearer the truth than Regnault's, we obtain the following results.

TABLE IV.—Absolute Zero from Chappuis' Pressure-Coefficients.

Gas employed .....	Nitrogen.	Hydrogen.	CO <sub>2</sub> .
Pressure-Coefficient ( $p_0=100$ cms.), $a$ .	·0036747	·0036625	·0037251
Fundamental Zero of Gas, $T_0=1/a$ ...	272°·11	273°·03	268°·45
Correction to Absolute Zero, $\theta_0 - T_0$ ...	+0°·98	+0°·11	+5°·55
Absolute Zero deduced, $\theta_0$ .....	273°·09	273°·14	274°·00

These evidently agree very closely with the results deduced for the same gases from Regnault's expansion-coefficients. The cooling-effect for nitrogen was found by Joule and Thomson to be larger than for air in the proportion of 103 to 88. I have allowed for this in Table IV. and also in Table VI. as it gives a better agreement with experiment on the assumption  $n=2$ . But Joule and Thomson did not regard their experiments on nitrogen with much confidence,

and the true value of  $n$  is probably more nearly 1.5 for diatomic gases (see below, section 20). The value found for  $\text{CO}_2$ , namely 274.0, differs from that calculated by the direct method of formula (22), which is certainly correct. The explanation of this apparent discrepancy is given below in section 15.

The values of the scale-correction for the same gases, calculated by formulæ (41) and (43) with the values of the constants given in Table II., deduced from the observations on the cooling-effect alone on the assumption  $n=2$ , are given in the following table. The table covers a wide range of temperature, and is intended to illustrate the general effect of the correction, but it must be remembered that the observations on which it rests were confined to the range  $0^\circ$  to  $100^\circ \text{C}$ .

TABLE V.—Scale-Correction for Air,  $\text{H}_2$ , and  $\text{CO}_2$ .

Temp. Cent.	Constant-Volume, $p_0=76$ cms.			Constant-Pressure, 76 cms.		
	Air.	Hydrogen.	$\text{CO}_2$ .	Air.	Hydrogen.	$\text{CO}_2$ .
$-200^\circ$	...	+109	...	...	+586	
$-150$	+258	+040	...	+1.02	+158	
$-100$	+099	+015	...	+328	+050	
$-50$	+029	+005	+22	+086	+015	+85
$-20$	+0080	+0012	+062	+022	+0035	+172
$-10$	+0036	+0006	+027	+010	+0017	+076
$+10$	-0027	-0004	-0207	-0073	-0011	-056
$+20$	-0046	-0007	-0356	-0122	-0019	-095
$+30$	-0059	-0009	-0452	-0155	-0024	-119
$+40$	-0065	-0010	-0500	-0169	-0026	-130
$+50$	-0066	-0010	-0504	-0170	-0026	-130
$+60$	-0061	-0009	-0470	-0155	-0025	-120
$+70$	-0052	-0008	-0398	-0132	-0020	-101
$+80$	-0039	-0006	-0295	-0098	-0015	-074
$+90$	-0021	-0003	-0162	-0052	-0008	-040
$+150$	+015	+002	+115	+036	+006	+274
$+200$	+036	+006	+275	+083	+013	+635
$+300$	+089	+014	+683	+196	+031	+151
$+450$	+186	+029	+142	+392	+061	+300
$+1000$	+600	+093	+460	+116	+181	+893
$+2000$	+142	+221	+109	+262	+407	+202

### 9. Comparison with Chappuis' Experiments.

It is interesting to compare the results calculated in this table with the experiments of Chappuis (Bureau Internat. Reports, 1888) on the differences between the scales of the nitrogen, hydrogen, and carbonic acid gas-thermometers. The most accurate and important of his experiments were made with the constant-volume thermometer at an initial pressure of 100 cms. The gas-thermometers were not directly compared, but the same instrument was employed successively with the different gases, and the readings at intervals of 5° up to 50° C., and also at 61° and 78°, were compared with those of four standard mercury thermometers.

The results of the comparisons of the mercury thermometer ( $t_m$ ) with the nitrogen and hydrogen thermometers ( $t_n$  and  $t_h$ ) were represented by the following empirical formulæ:—

$$t_n - t_m = t(100 - t)(-55.541 + 0.48240t - 0.0024807t^2) \times 10^{-6},$$

$$t_h - t_m = t(100 - t)(-61.859 + 0.47351t - 0.0011577t^2) \times 10^{-6}.$$

In order to make a comparison with Joule and Thomson it is necessary to take the difference between the nitrogen and hydrogen scales by subtracting the second formula from the first, which gives the expression

$$t_n - t_h = t(100 - t)(+6.318 + 0.00889t - 0.0013230t^2) \times 10^{-6}. \quad (44)$$

This is the formula which is generally quoted for the difference between the nitrogen and hydrogen scales; but it must be remembered that it refers to an initial pressure of 100 cms. at constant volume, and that it is obtained as the difference between two comparisons with the mercury thermometer, which may have introduced small constant errors, especially at the higher points of the scale. The differences calculated by formula (44) are compared with those taken from Table V., corrected from air to nitrogen by the factor 103/88, and increased in the proportion 100/76 to reduce to 100 cms. initial pressure, under the heading  $n=2$ , in the following table, together with later reductions.

TABLE VI.—Difference between Scales of Constant-Volume Nitrogen and Hydrogen Thermometers  $t_n - t_h$  at 100 cms. initial pressure.

Temp. Cent.	Joule-Thomson.		Chappuis *.		Lehfeldt, Phil. Mag. 1898.	Rose-Innes, Phil. Mag. 1901.
	$n=1.5$ .	$n=2$ .	Formula (44).	Corrected 1888.		
-20	-.0085	-.0107	-.0135	-.0173		
-10	-.0080	-.0048	-.0067	-.0074		
+10	+.0022	+.0036	+.0057	+.0053	+.006	+.0010
+20	+.0040	+.0060	+.0095	+.0087	+.011	+.0018
+30	+.0049	+.0077	+.0113	+.0105	+.014	+.0023
+40	+.0055	+.0087	+.0110	+.0110	+.017	+.0025
+50	+.0055	+.0087	+.0088	+.0103	+.019	+.0025
+60	+.0050	+.0078	+.0049	+.0090	+.019	+.0024
+70	+.0045	+.0064	+.0010	+.0069	+.018	+.0020
+80	+.0034	+.0048	-.0024	+.0045	+.015	+.0015
+90	+.0018	+.0028	-.0032	+.0022	+.010	+.0008

It will be observed that formula (44) gives negative values of the difference  $t_n - t_h$  at 80° and 90° C.; but these are of the same order as the probable error of observation, which was .003° or .01 mm. Hg. The only observation actually taken at this part of the scale, namely, at 78° C. in the vapour of alcohol, shows a small positive difference of .001°. The negative differences are undoubtedly due in part to the type of empirical formula chosen. Chappuis himself considered them to be impossible, because they imply that the mean coefficient of expansion of nitrogen, after diminishing from 0° to 70° C., begins to increase again at this point, which is highly improbable. For this reason, in the same paper in which formula (44) is given, he calculated another formula, with two terms instead of three, for deducing the mean coefficient of expansion of nitrogen by reference to hydrogen. He does not give the values of the scale-difference corresponding to this formula, but I have calculated the values given in the column headed "Corrected 1888" from the values which he tabulates of the mean coefficient of expansion of nitrogen. It is at once evident that the formula of two

\* Chappuis' latest observations ('Bureau Internat. Reports,' 1902) make the difference  $t_n - t_h = +.005$  at 20°, and  $+.008$  at 40° C., which agree better with Joule and Thomson.

terms gives a more probable type of divergence between the scales than the three-term formula (44) which is always quoted. It agrees closely with that of Joule and Thomson at the higher points, but gives rather larger differences at the lower points, increasing to nearly double at  $-20^{\circ}\text{C}$ .

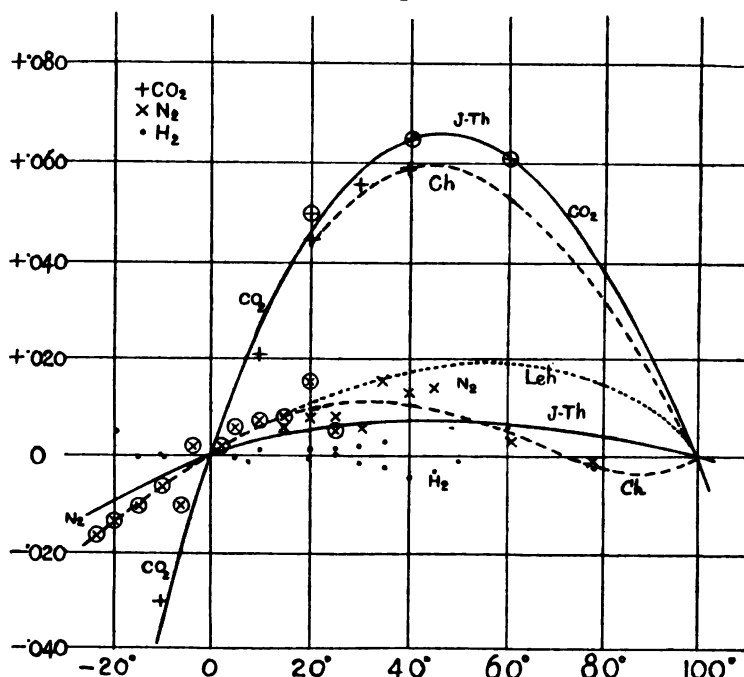
#### 10. *Graphic Method of Comparison.*

Since the thousandths of a degree in this table are uncertain to the extent of at least  $\cdot 003^{\circ}$ , it is hardly necessary to say that the most that can be expected is a general agreement in the order of magnitude of the correction. The value of the experimental evidence is most readily appreciated by the graphic method. The actual observations are plotted in fig. 1, in which the zero line represents the hydrogen scale, and the ordinates of the curves the scale-differences. The continuous curves represent the differences calculated from the observations of Joule and Thomson, the broken curves the differences calculated from the formulæ of Chappuis. The black dots about the zero line represent the deviations of the observations with the hydrogen thermometer from the smooth formula chosen to represent them, and indicate the order of accuracy of the comparison of the hydrogen and mercury thermometers. The crosses ( $\times$ ) similarly indicate the divergences of the observations with the nitrogen thermometer from the smooth curve. The crosses inclosed in circles represent the observations in the second series of comparisons of the nitrogen thermometer, extending from  $-24^{\circ}$  to  $+25^{\circ}\text{C}$ . In reducing these observations it was found that the curve representing them did not pass through the zero point, as of course it should. Chappuis assumed that this discrepancy was due to an error in the zero pressure, which had to be determined separately under conditions different from those of the thermometric comparisons. A reduction of  $\cdot 025\text{ mm.}$  in the zero pressure\* was required to make the curve pass through the origin. This correction had the effect of raising all the observations by nearly  $\cdot 007^{\circ}$ , which is a quantity of the same

\* The minuteness of this correction (1 in 40,000 on the zero pressure) indicates the extreme difficulty of the work, which could not have been carried out successfully without the highest experimental skill and the most refined apparatus.

order as the difference between the nitrogen and hydrogen scales. If the circled observations in the figure were depressed by  $\cdot 007^\circ$ , it is evident that they would be brought into rather better agreement with the Joule-Thomson curve between  $0^\circ$  and  $25^\circ \text{C.}$ , but that the discrepancy below  $0^\circ \text{C.}$  would be

Fig. 1.—Comparison of Chappuis' Observations with Results calculated from Cooling-Effect.



increased. The nitrogen observations are seen to be rather more discordant than the hydrogen, but they were taken first in point of time, and the error of the temporary rise of zero produced in a mercury thermometer by exposure to a low temperature (corresponding to the temporary depression produced by exposure to a high temperature), was discovered for the first time in the course of this series of observations. Taking these facts into consideration, we may conclude that the difference of the scales between  $0^\circ$  and  $50^\circ$  is probably less than that given by Chappuis' formula, and that the

Joule-Thomson curve is more nearly correct, though, as we shall see, there is other evidence tending to show that even the latter is too high.

### 11. *Extrapolation to Higher and Lower Temperatures.*

Since the observations of Joule and Thomson were confined to the range  $0^{\circ}$  to  $100^{\circ}$  C., the estimates of the corrections given in Table V. (p. 301) are liable to much greater uncertainty beyond this range, since they depend on the validity of the type of equation (39) assumed. According to the table, the difference between the scales of the constant-volume and the constant-pressure hydrogen thermometers would be about half a degree at the temperature of liquid air. This has been recently confirmed by Travers (B. A. Rep. 1901), and may be taken as an indication that the divergence indicated in the table is at least of the right order of magnitude, even in the case of hydrogen. Similarly the corrected value of the boiling-point of sulphur given by Chappuis (Phil. Mag. 1902), namely  $444^{\circ}7$ , obtained with a constant-volume nitrogen thermometer at 56 cms. initial pressure, when compared with the value  $444^{\circ}5$  obtained with a constant-pressure air-thermometer (Phil. Trans. 1891) agrees in sign and order of magnitude with the difference of the scales ( $0^{\circ}2$ ) at this point indicated in the table. Chappuis has recently proposed an empirical method of estimating the correction, which leads to a much smaller result. His original formula (44) is evidently of a type unsuitable for extrapolation; but if we employ it to calculate the true coefficient of expansion of nitrogen at  $t$ , assuming hydrogen to be an ideal gas, we find that the coefficient diminishes from  $\cdot00367698$  at  $0^{\circ}$  C. to  $\cdot00367378$  at  $80^{\circ}$  C., and then increases to  $\cdot00367393$  at  $100^{\circ}$  C. Chappuis supposes that this increase is illusory, and that the coefficient really diminishes to a minimum value, namely  $\cdot00367378$ , and then remains constant at all higher temperatures. This assumption would make the scale-difference linear above  $100^{\circ}$  C., increasing by  $\cdot017^{\circ}$  for each  $100^{\circ}$ , and amounting to  $\cdot076^{\circ}$  at the boiling-point of sulphur for a constant-volume thermometer at 100 cms. initial pressure, or  $\cdot048^{\circ}$  for  $p_0=56$  cms. He finds, as the result



of some experiments between  $0^{\circ}$  and  $100^{\circ}$ , that the scale-correction of the constant-pressure thermometer is about twice that of the constant-volume instrument. This agrees very fairly with the result deduced from the Joule-Thomson equation and exhibited in Table V. Assuming the ratio 2, the correction for the constant-pressure thermometer at  $44.5^{\circ}$  would be about  $+0.115^{\circ}$  at 76 cms. initial pressure, which would give a difference of  $0.072^{\circ}$  between our instruments at the boiling-point of sulphur. Chree has since detected a small error in Chappuis' calculation which would increase this estimate in the proportion of  $0.023$  to  $0.017$ . A direct comparison between the constant-volume and constant-pressure scales at this temperature would certainly be desirable and feasible; but in the meantime the estimate derived from the Joule-Thomson equation appears to be more probable than that of Chappuis, and more in accordance with the known behaviour of gases deduced by other methods of investigation.

#### 12. *Thermodynamical Correction of $\text{CO}_2$ Thermometer.*

The case of  $\text{CO}_2$  is of particular interest because the properties of this gas have been so widely studied, and because the deviations from the thermodynamical scale and the values of the Joule-Thomson effect are so much larger and more easily measured. A study of the properties of this gas might be expected to throw light on the effects to be expected with other gases more perfect and better suited to thermometry; but it must not be forgotten that the type of the molecule is different, and that for this reason it might be expected to behave in a different manner to the diatomic or monatomic gases. The gas actually employed by Joule and Thomson was not quite pure, but they corrected their results empirically to the case of pure gas, and their value of the cooling-effect at  $17^{\circ}\text{C.}$  has been independently confirmed by Natanson (Wied. Ann. xxxi. p. 502, 1887) employing gas from cylinders of liquid  $\text{CO}_2$ . The values given by Table V. for the difference from the hydrogen scale in the case of the constant-volume thermometer at  $p_0=100$  cms. are compared with the observations of Chappuis at  $-10^{\circ}$ ,  $+10^{\circ}$ ,  $20^{\circ}$ ,  $30^{\circ}$ ,  $40^{\circ}$ , and  $60^{\circ}\text{C.}$ ,

which are represented by the crosses (+) in fig. 1. The full curve, as before, indicates the differences calculated by the Joule-Thomson equation, the broken curve indicates the formula of Chappuis. Three of Chappuis' observations at  $30^\circ$ ,  $40^\circ$ , and  $60^\circ$  were taken with a thermometer filled with gas at a slightly lower initial pressure,  $p_0=87$  cms. The observed values for the difference in these cases have been increased in the ratio  $100/87$ , as required by theory, and the crosses are distinguished by inclosing them in circles. It will be observed that the corrected observations agree in the most remarkable manner with the Joule-Thomson curve, although their agreement with Chappuis' formula is slightly impaired. This would appear to be a striking confirmation of the validity of the proposed formula in the case of  $\text{CO}_2$ . But when we compare the actual values of  $c$  and  $b$  calculated as above from the observations on the cooling-effect alone, with those calculated directly from the slope of the isothermals, we find certain discrepancies which, although they are often within the limits of experimental error, require examination as possible indications of some defect in the theory. For instance, in the case of  $\text{CO}_2$ , which agrees so well with Chappuis' thermometric comparisons, the value of  $c$  according to Table II. would become equal to that of  $b$  at about  $120^\circ \text{C.}$ , and the gas above this temperature should behave like hydrogen, with an upward slope of the isothermal. The observations of Amagat show, on the other hand, that  $\text{CO}_2$  is still notably imperfect at a temperature of  $261^\circ \text{C.}$  This might conceivably be due in part to some effect of surface-condensation, which would be relatively important in the fine tubes employed by Amagat; but it is mainly attributable to the large value of  $b$  deduced from the observations on the cooling-effect. It is evident that the value of  $b$  cannot be deduced so accurately as that of  $c$  from these observations, since the expression for  $\text{SQ}$  is  $3c-b$ . Moreover, no account has been taken of the variation of  $S$  with temperature, which according to Regnault is considerable in the case of  $\text{CO}_2$ . Both these considerations would be of relatively small importance as affecting the thermometric comparisons between  $0^\circ$  and  $100^\circ$ , since  $b$  does not enter into the expression for  $dt$ , and we employ the mean value of  $S$  at  $50^\circ$ ; but they would

materially affect the extrapolation of the value of  $c-b$ . It would be quite possible to readjust the values of  $c$  and  $b$  in such a manner as to agree better with Amagat at higher temperatures, while not seriously impairing the agreement with Chappuis at 50°. The values of  $c$  and  $b$  for hydrogen appear to be more nearly of the right order of magnitude, giving  $b-c=8.2$  c. c. as against Amagat's value 8.8 c. c. On the other hand, the value of  $b$  for air is practically zero according to the observations of Joule and Thomson, *i. e.* air would always remain imperfect. Observation shows, however, that it becomes "pluperfect" at a temperature somewhere below 100° C. Here again the value of  $b$  is undoubtedly in error. It may also be observed that the error of the value of the absolute zero deduced in Table IV. from Chappuis' pressure-coefficient for CO<sub>2</sub>, namely 274.0, is too large to be attributed to errors of observation in the coefficient or in the measurement of the cooling-effect. These discrepancies suggest either that the type of formula is wrong (*i. e.*, that  $c$  does not vary inversely as the square of the absolute temperature), or else that the variations of the specific heat are too large to be neglected.

### 13. *Other Types of Formulae* \*.

Instead of attempting to readjust the values of the constants in the original formula so as to obtain the best average agreement with experimental data, we might proceed, as suggested by Joule and Thomson in 1854 (Phil. Trans. p. 360), by the more usual method of introducing sufficient arbitrary constants into the formula to enable it to reconcile all the apparently discordant data. This method has recently been applied by Rose-Innes (Phil. Mag. July 1901), who adopts a formula with *three* constants, of the same type as that employed by Joule and Thomson, No. (11) above, in the calculation of their original table of corrections. But in place of Regnault's observations Rose-Innes adopts the later observations of Joule and Thomson on the cooling-effect, in conjunction with Amagat's values of  $d(pv)/dp$ . The values of  $t_{\infty}-t_2$  calculated by Rose-Innes are given in Table VI. (p. 303).

\* This section was added subsequently to the reading of the paper.

He does not apply his formula to the case of  $\text{CO}_2$ . The difference between the values of the absolute zero deduced by Rose-Innes from Chappuis' pressure-coefficients for  $\text{H}_2$  and  $\text{N}_2$  is rather larger than that given in Table IV., and would make the value lie somewhere between 273.15 and 273.36, which appears hardly probable.

To facilitate the comparison of the formulæ and the calculation of the corrections, we may employ the notation already explained in Section 8 above. The formula of Rose-Innes is equivalent to the assumption

$$\theta = pv/R + (c' + c'' - b)p/R, \quad . \quad . \quad . \quad (45)$$

in which  $c'$  and  $c''$  vary inversely as the first and second powers of the temperature respectively. The corresponding formulæ for the corrections are:—

Constant-volume, zero correction,

$$\theta_0 - T_0 = 646 C'' + c_0' p_0/R, \quad . \quad . \quad . \quad (46)$$

Scale correction,

$$dt = C'' t(t-100)/\theta, \quad . \quad . \quad . \quad (47)$$

Constant-pressure, zero correction,

$$\theta_0 - T_0 = 846 C'' + 646 C' - b p_0/R, \quad . \quad . \quad . \quad (48)$$

Scale correction,

$$dt = (C''(1.732 + 273/\theta) + C')t(t-100)/\theta. \quad . \quad (49)$$

The formulæ are the same as before as regards  $c''$ , but additional terms are introduced to represent the effect of  $c'$ . The numerical values of the constants are given in the following table as deduced from those calculated by Rose-Innes.

TABLE VII.—Values of Constants deduced from Formulæ of Rose-Innes.

Gas employed.	$b$ . c.c.	$c_0'$ . c.c.	$c_0''$ . c.c.	$C'$ . $c_0' p_0/373R$ .	$C''$ . $c_0'' p_0/373R$ .
Air .....	1.62	1.89	0.182	.00179	.00017
Nitrogen ...	2.03	2.09	0.378	.00182	.00035
Hydrogen ...	10.73	1.19	1.45	.000078	.000095

The values of the scale-correction calculated by these

formulæ for the constant-volume air-thermometer are about five times smaller than those given in Table V., but the values for the constant-pressure thermometer are nearly of the same magnitude as those in Table V. In general we may observe that the corrections for the constant-pressure thermometer are nearly independent of the type of formula assumed within reasonable limits, and are therefore less uncertain than those of the constant-volume thermometer. The values of  $C'$  and  $C''$  given above correspond, as before, to an initial pressure  $v_0 = 76$  cms.

#### 14. *Variation of Specific Heats.*

The method followed by Joule and Thomson, and by the majority of subsequent writers, has been to assume a formula for the variation of the cooling-effect  $Q$ , which is then integrated to find the constants in the characteristic equation, neglecting the variations of the specific heat  $S$ . This is perfectly justifiable in the case of the more permanent gases, for which experiment and theory both indicate that the variations of the specific heat should be small. But in the case of vapours like steam or  $\text{CO}_2$ , these variations cannot be neglected; and it is better to employ the reverse method as in Section 7 above, assuming a convenient type of characteristic equation and deducing the corresponding expression for the cooling-effect for comparison with the results of observation. In this case it is easy to take account of the variations of the specific heat by simply inserting the appropriate value of the specific heat in equation (30).

We observe by reference to the differential equations (4) or (5) that the appropriate value of  $S$  is that corresponding to the final pressure  $p''$  in each experiment, and to the mean temperature  $(\theta' + \theta'')/2$ . The variation of the specific heat with temperature can be determined only by experiment. The variation with pressure must be consistent with the characteristic equation chosen, and can be calculated in the following manner.

Referring to equation (3) for the variation of the total heat,  $F = E + pv$ , we have the following values of the partial differential coefficients:—

$$(dF/d\theta)_p = S, \quad (dF/dp)_\theta = v - \theta(dv/d\theta)_p = b - (n+1)c, \quad (50)$$

which give for the variation of  $S$  with  $p$  at constant  $\theta$ ,

$$(dS/dp)_\theta = d_2 F/d\theta dp = -\theta(d_2 v/d\theta^2)_p = n(n+1)c/\theta. \quad (51)$$

Integrating this at constant temperature from 0 to  $p$ , we obtain

$$S = S_0 + n(n+1)cp/\theta, \quad \dots \quad (52)$$

where  $S_0$  is the limiting value of  $S$  at zero pressure and temperature  $\theta$ .

This equation enables us to find the complete variation of  $S$ , if we observe the values of  $S$  experimentally at any standard pressure such as 1 atmo, over the required range of temperature.

Proceeding similarly for the specific heat  $s$  at constant volume, we obtain by considering the variation of the intrinsic energy  $E$ ,

$$(dE/d\theta)_v = s, \quad (dE/dv)_\theta = \theta(dp/d\theta)_v - p, \quad (ds/dv)_\theta = \theta(d_2 p/d\theta^2)_v, \quad (53)$$

whence

$$s = s_0 + n(n-1-nc/V)cp/\theta, \quad \dots \quad (54)$$

where  $s_0$  is the limiting value of  $s$  at zero pressure, and  $V = R\theta/p$ . This formula is of comparatively little use, because the direct measurement of  $s$  by experiment is generally impracticable; but it serves to trace the probable variations of the ratio of the specific heats  $S/s = g$ .

In the special case in which  $n = s_0/R$  the formulæ may be somewhat simplified, since  $R = S_0 - s_0$ , and may be written as follows:—

$$S = S_0(1 + nc/V), \quad \dots \quad (55)$$

$$s = s_0(1 + nc/V)(1 - c/V), \quad \dots \quad (56)$$

whence

$$g = S/s = g_0/(1 - c/V). \quad \dots \quad (57)$$

This appears to be the case for steam (Proc. R. S. vol. lxvii. p. 266, 1900), but is not true generally.

In the case of a diatomic gas, if we assume the limiting ratio of the specific heats to be  $g_0 = 1.400$ , as indicated by theory, we have  $S_0 = 3.5R$ ,  $s_0 = 2.5R$ , if the limiting values of the specific heats are constant. The ratio of the specific heats, if  $n = 2.5$ , would be  $g = 1.400(1 + c/V)$ . If  $n = 2$ , as in Rankine's equation, we should have  $g = 1.400(1 + .92c/V)$

approximately. Inserting  $c_0 = 0.90$  c. c.,  $V = 784$  c. c. for air at  $0^\circ$  C. and 75 cms. pressure, we should find  $g = 1.4015$ , which illustrates the smallness of the variation with pressure for the permanent gases. Taking the density of air as  $1.2930$  gm. per litre at  $0^\circ$  C. and 760 mm. in lat.  $45^\circ$ , and assuming the value of  $c-b$  at  $0^\circ$  to be  $0.50$  c. c. from Amagat's observations, we should find  $R = 2.8725 \times 10^6$  c.g.s., which would give  $S = 3.5R = 1.0055$  joules per gramme-degree; or  $0.2405$  calories at  $20^\circ$  C., if the calorie at  $20^\circ$  C. is taken as  $4.180$  joules. This is about 1 per cent. larger than the value found by Regnault, namely  $S = .2375$ . The observations of Joly at constant volume give  $s = .1721$  cal. at  $60^\circ$  C. and  $v = 49$  c. c., when reduced to the same unit. The theoretical value at this pressure, assuming  $c = 0.61$  c. c. at  $60^\circ$  C., would be  $0.1736$  calories, which is also nearly 1 per cent. larger than that observed. It should be remarked, however, that even apart from the difficulty of the experiments, there is considerable uncertainty in the units of heat employed. Joly used Regnault's value for the latent heat of steam at  $100^\circ$ , namely  $536.7$ ; but his own experiments with the steam calorimeter give  $540.2$  in terms of the calorie at  $20^\circ$ . The difference is nearly sufficient to account for the discrepancy in the observed and calculated values. Considering the difficulty of experiments on the specific heats of gases, we are probably justified in the assumption that the limiting values of the specific heats are constant for the more permanent diatomic gases, and that the variations with pressure may be estimated by the formulæ already given.

#### 15. *Constants for $\text{CO}_2$ corrected for Variation of $S$ .*

In order to correct the values of  $c_0$  and  $b$  for  $\text{CO}_2$  calculated in Table II. from the observed values of  $Q$  on the assumption that  $S$  was constant and equal to  $8.4 \times 10^6$  c.g.s., we may take Regnault's values of  $S$  at  $0^\circ$  and  $100^\circ$  at a pressure of 1 atmo, since the final pressure in Joule and Thomson's experiments was always approximately atmospheric. The values of  $S$  required may be taken as

$$S_0 = 7.85 \times 10^6 \text{ c.g.s.}, \text{ and } S_{100} = 8.95 \times 10^6 \text{ c.g.s.};$$

but the absolute values, as well as the rate of variation, are

necessarily a little uncertain on account of the defects of Regnault's thermometry, and of the error of his formula for the variation of the specific heat of water.

Adopting the values of  $Q_0$  and  $Q_{100}$  given in Table II., and assuming  $SQ = 3c - b$ , we obtain the following values of the constants,

$$c_0 = 3.76 \text{ c. c.}, \quad b = 0.58 \text{ c. c.}$$

This would reduce all the values of the corrections for  $\text{CO}_2$  given in Table V. nearly in the proportion of 5 to 6, since they depend only on  $c_0$ . The agreement with Chappuis' observations\* plotted in fig. 1 would be slightly impaired, but the Joule-Thomson curve would coincide more nearly with Chappuis' empirical formula. The value of the absolute zero correction for the constant-pressure thermometer is scarcely altered; so that the value deduced from Chappuis' expansion coefficient is still correct. But on the other hand the zero correction for the constant-volume thermometer (Table IV.) by formula (40) is reduced in the proportion  $376/456$  from  $5^\circ.55$  to  $4^\circ.60$ , which gives  $\theta_0 = 273^\circ.05$ , thus agreeing with the direct method of calculation given in Section 5, formula (22).

If we compare the values of the compressibility deduced from the corrected values of the constants, with the values observed by Amagat, we find again the agreement much improved, which confirms the importance of the correction for the variation of the specific heat. It should be remarked, however, that the values of  $c - b$  deduced from Amagat's observations are a little uncertain, as the observations do not extend below a pressure of 50 atmos at  $100^\circ \text{ C.}$  The following table exhibits the comparison.

TABLE VIII.—Comparison with Amagat.

Temperature centigrade .....	$0^\circ.$	$100^\circ.$	$200^\circ.$
Values of $c - b$ calculated .....	3.18	1.44	0.67
„ „ observed.....	3.30	1.5	0.72

There is a small systematic difference which might possibly

\* More recent observations by Chappuis ('Int. Bureau Reports,' 1902) make the scale-correction for  $\text{CO}_2$  at  $p_0 = 100 \text{ cms.}$ ,  $+0.39^\circ$  both at  $20^\circ$  and  $40^\circ \text{ C.}$  instead of  $.043^\circ$  and  $.059^\circ$ .



be explained by surface condensation, but is hardly beyond the limits of uncertainty of the data.

It is possible by means of formula (54) to make a rough estimate of the variation of the specific heat of  $\text{CO}_2$  at constant volume for comparison with the experiments of Joly. Neglecting the small term  $nc/V$ , and putting  $n=2$ , the formula may be written approximately  $s=s_0+2Rc/V$ , where  $V=v+c-b$ . Joly's observations give for  $v=87$  c.c.,  $s=.1684$ ; and for  $v=27$  c.c.,  $s=.1734$ . These values are in calories, and correspond to a mean temperature of  $55^\circ \text{C}$ . The mean value of  $c$  may be taken as  $2.61$  c.c., so that  $2Rc=9.8 \times 10^6$  c.g.s. The values of  $V$  are  $89$  and  $29$  c.c. respectively, so that the calculated difference between the values of  $s$  comes out  $0.228 \times 10^6$  c.g.s., or  $0.0054$  calorie. The observed difference is seen to be  $0.0050$  calorie, which agrees quite as well as could be expected with the calculated value. It should be observed, however, that if we extrapolate to zero pressure, we find the limiting value of the specific heat  $s$  from Joly's observations about  $0.1655$  calorie per gramme-degree. The corresponding value for  $S$  from Regnault's observations at  $55^\circ \text{C}$ . is  $0.2014$ . The difference of these is only  $0.0359$  cal., or  $1.51 \times 10^6$  c.g.s., whereas the value of  $R$  is  $1.887 \times 10^6$  c.g.s. The discrepancy is nearly 5 per cent. of the value of  $S$  instead of only 1 per cent. as in the case of air.

#### 16. *Application of the Method to Steam.*

The large range of variation of the specific heat of  $\text{CO}_2$  with temperature shows that the molecule must undergo some fundamental change of structure within the limits of temperature considered. It is possible that this may be associated with the variation of the specific heat of carbon itself. There is no evidence of a similar variation in the case of the diatomic gases. In the case of steam, which is also triatomic, large variations of the specific heat, from  $S=.387$  at  $100^\circ \text{C}$ . to  $S=.665$  at  $160^\circ \text{C}$ ., have been found experimentally by Grindley, employing the Joule-Thomson method (Phil. Trans. A, 1900), and assuming Regnault's formula for the total heat of saturated steam. The following values have also been deduced by other writers on theoretical grounds: Zeuner,  $S=.568$ ; Gray,  $0.385$ ; Tumlriz,  $0.536$  to  $0.475$ ;

Perry, 0.306 to 0.463. I find, however, by direct experiment, employing the continuous electrical method with a vacuum-jacket calorimeter, the value  $S=0.497$  at 1 atmo and  $108^{\circ}$  C., which agrees fairly with Regnault's value 0.475 at  $175^{\circ}$  C., allowing for the variation due to the coaggregation by formula (52). I have endeavoured to show (Proc. R. S. lxvii. p. 266, 1900) that all the properties of steam may be consistently calculated on the assumption that the limiting value of the specific heat is constant, employing the same type of equation as for  $\text{CO}_2$ , but leaving the value of  $n$  to be determined from observations of the cooling-effect at various temperatures. If we adopt this type of formula, it appears from the observations of Grindley (Phil. Trans. 1900) that the value of  $n$  for steam should be about 3.8 instead of 2. My own observations on the cooling-effect and the specific heat of steam would give the values  $n=3.3$ , and  $c=26.3$  c.c. at  $100^{\circ}$  C. In calculating the properties of steam by this formula in the paper above referred to, I adopted the mean value 3.5 for the index, partly to facilitate calculation and partly in consequence of an hypothesis (doubtfully attributed to Maxwell) that the number of degrees of freedom of a molecule containing  $m$  atoms is  $2m+1$ . This hypothesis would make the ratio of the specific heats  $S/s$  at constant pressure and volume,  $5/3$  for a monatomic gas,  $7/5$  for a diatomic gas,  $9/7$  for a triatomic gas, and so on; values which agree very fairly with the ratios of the specific heats actually observed in many cases. Later and more accurate experiments on the specific heat of steam have shown that the ratio  $s/R$  should be more nearly 3.3, and have so far confirmed the value of the index given by my experiments on the cooling-effect.

Adopting the experimental value  $S=0.497$  at 1 atmo and  $108^{\circ}$  C. we find by applying formula (52) the limiting value  $S_0=0.478$  at zero pressure. If we employ this value in place of the value  $4.5R$  adopted on Maxwell's hypothesis in the paper above referred to, we find that the agreement with experiment in the values of the total heat and the saturation pressure is somewhat improved, but the general nature of the conclusions remains unaltered. Since the value of the index

$n$  cannot be determined very accurately from the cooling-effect, it is better in this case to take it equal to  $s/R$  for the sake of simplifying the equation of the isentropics, which then takes the form  $c/V = \text{constant}$ , or  $p/\theta^{n+1} = \text{constant}$ , or  $p^n(v-b)^{n+1} = \text{constant}$ .

In the case of steam the constancy of the specific heat, and the accuracy of the value found by experiment, may be further verified by calculating the values of the total heat and saturation pressure as follows :—

Adopting the assumption  $S_0 = \text{constant}$ , it is possible to express the thermodynamical properties of any imperfect gas or vapour in terms of  $c$  by means of very simple formulæ : thus we find

$$\text{Entropy, } \phi = S_0 \log_e \theta - R \log_e p - ncp/\theta + A, \quad (58)$$

$$\text{Energy, } E = s_0\theta - ncp + B, \quad (59)$$

in which  $A$  and  $B$  are indeterminate constants of integration. The values of the other thermodynamic functions follow immediately from those of  $E$  and  $\phi$ . Thus we find for the total heat

$$F = E + pv = S_0\theta - (n+1)cp + bp + B; \quad (60)$$

and for the thermodynamic potentials at constant pressure and volume,

$$G = F - \theta\phi = S_0\theta(1 - \log_e \theta) - R\theta \log_e p - (c-b)p - A\theta + B, \quad (61)$$

$$J = E - \theta\phi = s_0\theta - S_0\theta \log_e \theta - R\theta \log_e p - A\theta + B. \quad (62)$$

Observing that the difference of the total heats of the liquid and vapour at any temperature is equal to the latent heat  $L$ , and the difference of the entropies equal to  $L/\theta$  (or equating values of  $G$  for the liquid and vapour), we obtain the equation for the saturation-pressure,

$$R \log_e p = A' - B'/\theta - (s' - S_0) \log_e \theta + (c-b)p/\theta, \quad (63)$$

in which the specific heat  $s'$  of the liquid is assumed to be constant.  $A'$  is a constant to be determined by the observation of the boiling-point;  $B'$  is the difference of the constants  $B$  in the expressions for the total heats of the vapour

and liquid, which may be determined by the observation of the latent heat at the same point.

It should be observed that the equations for the thermodynamic potentials and for the vapour-pressure are independent of the assumption that  $c$  varies inversely as the  $n$ th power of the temperature, and are generally true provided that  $c-b$  is a function of the temperature only; but the assumption  $c=c_0(\theta_0/\theta)^n$  satisfies Regnault's observations of the saturation-pressure very accurately.

### 17. *Interpretation of the Index $n$ .*

Some idea of the meaning of the index  $n$  may be obtained by considering the expression above given for the Energy  $E$ . The energy of an imperfect gas is less than that of the gas in the ideal state at the same temperature by the term  $ncp$ , which represents the loss of energy due to coaggregation of the molecules, corresponding to the diminution of volume  $c$  per unit mass. Considering first the case of a monatomic gas, in which the whole of the kinetic energy of the molecules consists of energy of flight (corresponding to three degrees of freedom), we have the well-known relation  $pv = R\theta = 2s\theta/3$ . In a diatomic gas, regarded as consisting of pairs of atoms rigidly joined together like dumbbells, it appears probable, as suggested by Boltzmann, that the energy of a molecule may be equally distributed between each of *three* degrees of freedom of translation and *two* degrees of freedom of rotation, supposing that the rotation of a molecule about its axis could not be altered by intermolecular collisions. Such a molecule would have five equal degrees of freedom, and the specific heat at constant volume should be  $5R/2$ , which is amply confirmed by experiment. Supposing that two monatomic molecules each with three degrees of freedom coaggregate to form a diatomic molecule possessing five degrees of freedom, there would be a loss of energy equivalent to one degree of freedom, or one third of the energy of flight, since the energy of flight of the resulting diatomic molecule would be the same as that of a single monatomic molecule at the same temperature. If the diminution of volume per unit mass due to coaggregation be represented by  $c$ , the loss of energy on this

hypothesis would be represented by  $cp/2$ , since the product  $cp$  represents two-thirds of the energy of flight in a volume  $c$ . We ought therefore to have the index  $n=1/2$ , in the case of a monatomic gas, on the simple hypothesis of coaggregation in pairs, provided that the coaggregation is a purely physical effect, and that there is nothing in the nature of chemical combination involving evolution of heat.

In the case of a diatomic gas, a similar line of reasoning fails to give a definite result, because we have no sure experimental guide or mechanical analogy to enable us to estimate the number of degrees of freedom of the resulting tetratomic aggregate. If we supposed with Maxwell that the number of degrees of freedom could not exceed six, as for a rigid body, the loss of energy for a pair of diatomic molecules each possessing five degrees of freedom would be equivalent to four degrees of freedom on coaggregation, which would make the value of the index  $n=2$ , as in the Joule-Thomson equation. There can be no doubt, however, from experimental evidence, that the energy of flight may be less than half the total kinetic energy of a polyatomic molecule, otherwise the ratio  $S/s$  of the specific heats could not be less than  $4/3$ . It is probable that the distribution of energy in the molecule depends on the type or form of the molecule, and not merely on the number of atoms it contains, and that the various degrees of freedom are not all of equal value. The ratio of the energy of rotation  $E''$  to the energy of flight  $E'$  in the case of  $\text{CO}_2$  is about  $4/3$ , corresponding to the ratio of specific heats  $S/s=9/7$ . Whence, if  $n=2$ , the ratio  $E''/E'$  should be  $7/3$  for a coaggregated pair of molecules. For steam, which is also a triatomic molecule, the loss of energy on coaggregation is greater. We have  $n=3\cdot3=s/R$ , so that the whole energy of a coaggregated pair is no greater than that of a single molecule. It is further possible that the relative importance of the different kinds of degrees of freedom in a complicated molecule would vary with the temperature. We could not then assume that the limiting value  $S_0$  of the specific heat at zero pressure was constant. The assumption  $S_0=\text{constant}$  is almost certainly true for monatomic or diatomic molecules at ordinary temperatures; but it could not

be true for unstable molecules, and there is some evidence that it does not hold for polyatomic molecules of higher orders.

### 18. *Application to Monatomic Gases.*

The only observations so far available to test the hypothesis  $n=1/2$  in the case of monatomic gases, are those of Ramsay and Travers (Phil. Trans. A, 1901) on the compressibility of the inert gases by the capillary-tube method at  $11^{\circ}2$  C. from 20 to 80 metres pressure, and at  $237^{\circ}3$  C. from 30 to 80 metres. These observations are not very suitable for the purpose, as they do not extend to low pressures. They also exhibit, as the authors point out, several anomalies, which may be due to some hitherto unexplained peculiarities in the behaviour of monatomic gases, or perhaps merely to experimental errors. The curves representing the variations of  $pv$  with  $p$  at the lower temperature are of a perfectly normal type, the gases helium, neon, argon, krypton, and xenon, following naturally in the order of their densities. It should be remarked, however, that if we produce the curves for argon (39.9 gm.) and krypton (81.5 gm.) to zero pressure, they appear to indicate a limiting value of  $pv$  equal to 18,500 metre cubic centimetres approximately, whereas molecular weights of the other gases appear to conform to the limit 17,710 m.c.c., which is given as the ideal value for a perfect gas. At the higher temperature, the order of the gases is inverted. Helium and neon appear to be more imperfect than at the lower temperature, and their curves lie below krypton and argon. It seems to be impossible to offer any theoretical explanation of these anomalies; but if we admit that the limiting values for krypton at zero pressure should be 18,510 m.c.c. at  $11^{\circ}2$  C., and 33,240 m.c.c. (the corresponding value for the same mass of gas) at  $237^{\circ}3$  C., the limiting values of the slope ( $c-b$ ) may be estimated as 0.84 c.c. and 0.43 c.c. respectively per gramme of gas. In the case of the other gases the slope is too small, or its initial value too uncertain, to afford a comparison. If we assume as above that the coaggregation  $c$  should vary inversely as the square root of the temperature ( $n=1/2$ ), we find  $c=1.61$  c.c. at

284°·2 Abs. and  $c=1\cdot20$  c. c. at 510°·3 Abs., whence  $b=0\cdot77$  c. c. If on the other hand we assumed  $n=1$ , we should find  $c=0\cdot52$  c. c. at 510°·3 Abs., and  $b=0\cdot09$  c. c. A higher value such as  $n=2$  would make  $b$  large and negative, which would be impossible, or at least incapable of rational interpretation. The volume of liquid krypton at its boiling-point was found to be 0·46 c. c. per gramme, so that the value of  $b$  deduced on the assumption  $n=1/2$  is perhaps the most probable. The fact that helium appears to be less perfect than hydrogen, and neon nearly as imperfect as nitrogen at 11°·2 C., also supports the hypothesis of a very low value of  $n$  for monatomic gases.

Adopting provisionally the basis  $n=1/2$ , I have calculated the following tables of corrections for argon and helium in addition to krypton, since, as I have previously explained (Phil. Mag. Dec. 1899, p. 541), the inert monatomic gases are peculiarly suitable for thermometric purposes. I have assumed the values of  $b$  for helium and argon to be equal to the volumes of the liquids (which are estimated at 3·3 c. c., and 0·83 c. c. respectively) multiplied by the ratio  $0\cdot77/0\cdot46$  found above in the case of krypton. The values of  $c$  are deduced from the observed compressibilities at 11°·2 C. For helium I have assumed  $c_0=b$ , since the  $pv$  line for helium is practically horizontal up to a pressure of 50 metres. It must be admitted that these data are somewhat uncertain, but they afford at least a reasonable basis for comparison with experiment.

TABLE IX.

Values of Constants assumed for Monatomic Gases.

Gas employed.	$c_0$ c. c.	$b$ c. c.	$c_0-b$ c. c.	$R$ $\times 10^{-6}$	$S$ $\times 10^{-6}$	Factor $c_0 p_0/R$ .	
						76 cms.	100 cms.
Krypton...	1·64	0·77	0·87	1·064	2·66	1·567	2·063
Argon.....	2·18	1·39	0·79	2·175	5·43	1·016	1·337
Helium ...	5·5	5·5	0·00	20·8	52·0	0·268	0·352

Assuming the value  $n=0.5$ ,  $c=c_0(\theta_0/\theta)^{0.5}$ ,  $c_0-c_1=0.1445\,c_0$ , we have the following formulæ for the zero correction :—

Zero Correction, Constant-Pressure,

$$\theta_0 - T_0 = (c_0 - b + 2.73 \times 0.1445 \times c_0)p_0/R,$$

”      ”      Constant-Volume,

$$\theta_0 - T_0 = 3.73 \times 0.1445 \times c_0 p_0/R,$$

from which we deduce the values of the expansion- and pressure-coefficients given in the following table, assuming the value  $\theta_0=273^\circ.10$  :—

TABLE X.

Expansion- and Pressure-Coefficients for Monatomic Gases.

Gas employed.	Constant-Pressure, 76 cms.			Constant-Volume, $p_0=100$ cms.		
	$\theta_0 - T_0$ .	$T_0$ .	$1/T_0$ .	$\theta_0 - T_0$ .	$T_0$ .	$1/T_0$ .
Krypton ...	1.52	271.65	.0036812	1.11	272.00	.0036761
Argon .....	0.77	272.33	.0036717	0.72	272.38	.0036710
Helium .....	0.10	273.00	.0036628	0.19	272.91	.0036640

The value of the pressure-coefficient observed by Travers (Proc. R. S. lxx. p. 485) for helium at a mean initial pressure of 60 cms. is from .0036624 to .0036631, mean .0036627. The calculated value at this pressure would be .0036632, which is within the limits of possible error, but may indicate that the value of  $c$  assumed is too large.

The values of the scale-correction for the monatomic gases given in Table XI. are calculated by the following formulæ :—

$$\text{Constant-Pressure, } dt = (0.1445\,t/100 - 1 + (\theta_0/\theta)^{0.5})c_0 p_0/R,$$

$$\text{Constant-Volume, } dt = (-0.1689\,t/100 - 1 + (\theta/\theta_0)^{0.5})c_0 p_0/R.$$



TABLE XI.  
Scale-Correction for Monatomic Gases.

Temp. cent.	Constant-Pressure, 76 cms.			Constant-Volume, $p_0 = 100$ cms.		
	Krypton.	Argon.	Helium.	Krypton.	Argon.	Helium.
-250	...	...	+0.557	...	...	-0.101
-200	...	...	+ .173	...	-.194	-.051
-150	...	+ .278	+ .073	- .158	-.101	-.0285
-100	+ .175	+ .114	+ .0298	- .072	-.047	-.0123
-50	+ .053	+ .034	+ .0091	- .0242	-.0157	-.0041
-20	+ .0155	+ .0101	+ .00265	- .0070	-.0045	-.00120
-10	+ .0069	+ .0045	+ .00118	- .0031	-.0020	-.00053
+ 10	- .0052	-.0034	- .00089	+ .0027	+ .0017	+ .00045
+ 20	- .0083	-.0060	- .00159	+ .0045	+ .0029	+ .00077
+ 30	- .0116	-.0075	- .00198	+ .0058	+ .0038	+ .00098
+ 40	- .0130	-.0084	- .00222	+ .0064	+ .0041	+ .00109
+ 50	- .0130	-.0084	- .00222	+ .0065	+ .0042	+ .00113
+ 60	- .0124	-.0080	- .00212	+ .0062	+ .0040	+ .00106
+ 70	- .0105	-.0068	- .00180	+ .0056	+ .0036	+ .00095
+ 80	- .0078	-.0051	- .00133	+ .0041	+ .0027	+ .00070
+ 90	- .0042	-.0027	- .00072	+ .0021	+ .0014	+ .00035
+ 150	+ .0315	+ .0204	+ .0054	- .0180	-.0116	-.00306
+ 200	+ .075	+ .049	+ .0128	- .045	-.029	-.0076
+ 300	+ .194	+ .126	+ .0332	- .119	-.077	-.0203
+ 450	+ .415	+ .269	+ .071	- .275	-.178	-.0468
+ 1000	+ 1.42	+ .92	+ .243	- 1.09	-.71	-.187

It will be observed that the correction is negative for the constant-volume thermometer at temperatures below  $0^{\circ}\text{C}$ . According to Travers (*loc. cit.*) the helium thermometer reads  $0^{\circ}\cdot 1$  above the hydrogen thermometer at the boiling-point of oxygen, and  $0^{\circ}\cdot 2$  above at the boiling-point of hydrogen. The hydrogen correction is opposite in sign, and nearly equal in magnitude. The true values of the boiling-points, obtained by interpolating between the hydrogen and helium values, would be

Oxygen B.-P.  $90^{\circ}\cdot 13$  Abs.      Hydrogen B.-P.  $20^{\circ}\cdot 31$  Abs.

#### 19. Variation of the Covolume b.

Van der Waals, in his essay on the Continuity of State (Phys. Soc. Translation, 1890, p. 372), gives a theoretical

discussion of the effect of the size of the molecules on the length of the free path, from which on certain simple assumptions he deduces that for moderate pressures the effect may be represented by attributing to the covolume  $b$  a value equal to four times the actual volume of the molecules regarded as spheres. The theory indicates, however, that the value of  $b$  should diminish with increase of pressure somewhat rapidly when the volume approaches the value  $2b$ . He verifies this by applying his equation to represent the behaviour of  $\text{CO}_2$ , as observed experimentally by Andrews. Adopting for the constant  $a$  in his equation the value  $\cdot 00874$  (the unit of pressure being 760 mm. and the unit of volume the volume of the gas at  $0^\circ \text{C}$ . and 760 mm.) he finds values of  $b$  ranging from  $\cdot 0023$  to  $\cdot 0025$  for the vapour, but falling to  $\cdot 0016$  and  $\cdot 0018$  for the liquid. It appears both on theoretical and experimental grounds that  $b$  cannot be regarded as constant for a large range of pressure, and that no weight can be attached to calculations of the critical temperature based on the assumption that  $b$  is the same, as in van der Waals' equation, for both vapour and liquid. It nevertheless appears probable that the range of variation of  $b$  is not large, and that its value for moderate pressures is nearly constant with respect to both temperature and pressure. The value of  $b$  cannot be determined theoretically, because the actual volume of the molecules is unknown, and because the theoretical assumptions on which the estimate of the ratio 4 is based are extremely uncertain. Meyer, adopting a slightly different assumption, finds that  $b$  should be  $4\sqrt{2}$  times the volume of the molecules. If we assumed, as many writers have supposed, that the molecules of the liquid at low temperatures are practically in contact, and that the volume of the liquid in this case may be taken as the volume of the molecules, we should find, if we multiply by the factor 4 or  $4\sqrt{2}$ , values of  $b$  which are much too large to be reconciled with the observed behaviour of gases at moderate pressures. We may, however, assume with some degree of confidence that the volume of the liquid, or the limiting volume of the gas at very high pressures, is a limit below which the value of  $b$  at moderate pressures cannot greatly fall; and we may with propriety reject formulæ or experiments which lead to

much lower values. The limiting volumes of hydrogen and  $\text{CO}_2$  at high pressures are given by Amagat as 8.7 c. c. and 0.86 c. c. respectively, which are evidently quantities of the same order of magnitude as the volumes of the liquids. The difficulty in the determination of  $b$  from experiments at moderate pressures lies in the fact that it is of the order of a tenth of one per cent. of the volume of the gas at atmospheric pressure, that it cannot be determined independently of  $c$ , and that the values of both  $b$  and  $c$  depend on small differences between larger quantities in which the errors of observation are often of the same order as  $b$  itself. Boltzmann (*Gas-Theorie*) and van der Waals (*Arch. Néer.* iv. p. 299, and vi. p. 47, 1901) have recently given formulæ for the variation of  $b$  with pressure, which might theoretically be applied to correct the values of  $b$  obtained from observations at higher pressures so as to deduce the values at atmospheric pressure required for the correction of the gas thermometer or for the behaviour of gases at moderate pressures. But the development of these formulæ rests on assumptions even more uncertain than the discordant estimates of Meyer and van der Waals, and the range of variation indicated (Boltzmann says it is probably not greater than 1 to 10), would make the extrapolation of such formulæ very doubtful. It seems better to adopt a formula of the type already quoted, and to determine  $c$  and  $b$  from observations of the compressibility or the cooling-effect on the assumption that  $b$  is constant. The application of this method appears to lead to the conclusion that the value of  $b$  at moderate pressures does not differ greatly, if at all, from the volume of the liquid at or below its boiling-point. In applying the equation to calculate the properties of steam, in which case  $b$  is so small compared with  $c$  that it cannot be determined with any accuracy, I have for this reason simply assumed  $b$  equal to the volume of the liquid, and then calculated the values of  $n$  and  $c$  from the observations on the cooling-effect. The error involved is necessarily small since the value of  $(n+1)c$  at the boiling-point in this case is more than a hundred times the assumed value of  $b$ .

With regard to the variation of  $b$  with temperature, we can learn nothing from theory, and the indications of experiment

cannot be interpreted with certainty. From an empirical point of view the assumption  $b = \text{constant}$  is the simplest, and since it appears to satisfy the observations better than any other simple assumption, it should be retained unless it is decisively disproved.

## 20. *Application to Diatomic Gases.*

The application of the theory to diatomic gases is of particular interest and importance on account of the general employment of hydrogen, nitrogen, and air in gas-thermometers. It also presents peculiar difficulties, as compared with the case of a less perfect gas like  $\text{CO}_2$ , because the deviations to be measured and compared are so much smaller, while the probable error of observation remains the same. For instance, in the case of the three gases above mentioned, the deviations from Boyle's law are of the order of one part in a thousand only per atmosphere, and the order of accuracy of measurements of the compressibility by the capillary-tube method does not reach  $1/1000$  except under the best conditions. The advantage of the porous-plug method is that the cooling-effect represents the whole deviation sought, but the order of accuracy of the individual observations of Joule and Thomson did not exceed 5 or 10 per cent. at the higher temperatures. One of the final series of observations on air at  $40^\circ \text{C.}$  differs from the smoothed curve by more than 5 per cent., and one of the observations on nitrogen at  $92^\circ \text{C.}$  differs from the other by about 20 per cent. The nitrogen was prepared by burning phosphorus in air, and the values of the cooling-effect exceeded those for air by about 20 per cent., whereas the compressibility of nitrogen is decidedly less than that of air. The formula of Rose-Innes, with three constants, was designed to reconcile this apparent discrepancy, but if we extrapolate it to lower temperatures we find that it makes the compressibility of nitrogen much greater than that of air at  $-100^\circ \text{C.}$ , which is certainly contrary to fact. In Tables IV. & V., I have made a rough allowance for the fact that the observed cooling-effect for nitrogen was greater than for air, but little or no weight can be attached to this estimate. Nor can we overlook the fact that Joule and Thomson con-

sidered their observations on nitrogen much less satisfactory than those on air.

*Air.*—In order to obtain a satisfactory measurement of the constants  $c$  and  $b$  and of their rate of variation with temperature, it is obviously necessary to make experiments over a much wider range of temperature, and especially at lower temperatures, where the deviations are much larger and more easily measured. The observations of Witkowski (Phil. Mag. xli. p. 288, 1896) on Air appear to be the only ones available for the purpose. His method consisted in filling two similar bulbs with air at the same pressure but at different temperatures. The quantities of air in the two bulbs were then compared by discharging them into eudiometers at atmospheric pressure and temperature. From these data he deduced the mean coefficient of expansion at the given pressure, and all the data required for constructing a diagram of the variations of  $pv$  with  $p$  at constant temperature. The method, though troublesome, is evidently capable of great accuracy. It avoids or minimizes the effects of surface-condensation, which are so great an objection to the more convenient capillary-tube method. Witkowski observes in fact that his method always gave lower measurements of compressibility than the capillary-tube method, amounting to about 0.5 per cent. at 15° and 90 atmos, which may probably be explained as due to surface condensation in the capillary-tube method. For our purpose it will suffice to take one of Witkowski's isothermals for air, namely that at  $-78^{\circ}3$  C., which appears to have been determined with especial care, and which is so nearly straight up to high pressures that it is easy to make an estimate of the initial value of  $dpv/dp$ , which gives:—

Air at  $-78^{\circ}3$  C.,  $c-b=1.47$  c. c.; at  $0^{\circ}$  C.,  $c-b=0.50$  c. c.

The values of  $c$  and  $b$  for air calculated from the cooling-effect alone, assuming  $n=2$ , namely,  $c_0=0.90$ ,  $b=-.002$ , give  $c-b$  at  $0^{\circ}$  C.  $=0.92$  c. c., whereas the value should be 0.50 c. c. to agree with Amagat's observations. The value at  $-78^{\circ}3$  C. would be 1.79 c. c., which is also greater than that found by Witkowski. Moreover the negative value of  $b$  cannot be interpreted, and would make the error of the cal-

culated compressibility much greater at higher temperatures. It is clear that the value of  $b$  requires emendation. If we retain the same type of formula with  $n=2$ , and calculate the values of  $c_0$  and  $b$  to satisfy the observed values of  $c-b$  above given, we find:—

$$n=2, c_0=1.01 \text{ c. c.}, b=0.52 \text{ c. c.}, Q_0=0^\circ.250, Q_{100}=0^\circ.110.$$

The value of  $b$  thus found is still too small; the values of the cooling-effect deduced are also smaller than the observed values, namely,  $0^\circ.271$  and  $0^\circ.147$ , and the air would not become "pluperfect" till  $105^\circ \text{C}$ .

A much better agreement between the cooling-effect and the compressibility is obtained by taking  $n=1.5$  in the formula. This is not improbable theoretically, as the number of degrees of freedom lost by two diatomic molecules (each possessing five degrees of freedom) in coaggregating should be less than for triatomic molecules like  $\text{CO}_2$ . It is most unlikely that the tetratomic aggregate would possess only six degrees of freedom. The value  $n=1.5$  implies the loss of three degrees of freedom, which is more likely, if we suppose for simplicity that the number lost must be an integer. We then obtain

$$n=1.5, c_0=1.48, b=0.98, Q_0=0^\circ.271, Q_{100}=0^\circ.135.$$

With these values air would become pluperfect at about  $90^\circ \text{C}$ ., and the value of  $b$  is not much smaller than the volume of the liquid at low temperatures. The agreement with the observations on the compressibility is very good over a wide range of temperature. The agreement with the observations of the cooling-effect is exact at  $0^\circ \text{C}$ ., and the difference at  $100^\circ \text{C}$ . does not exceed the possible error of the experiments. If we abandon the hypothesis of *integral* degrees of freedom for triatomic or tetratomic molecules, we might of course calculate the value of the index  $n$  so as to obtain a better average agreement with observation, but even from a purely empirical point of view it is a matter of great convenience to have a simple value for the index  $n$ , provided that it satisfies the observations within the limits of probable error. Moreover the hypothesis of Maxwell, which is supported by the experiments on monatomic and diatomic gases,

is so simple and helpful that it is desirable to retain it as far as possible.

In applying the formula with the value  $n=1.5$  to determine the zero-correction and the scale-correction, the simplest method of proceeding is to find  $q$  for each temperature, and apply formulæ (34) and (36). The results for the constant-pressure thermometer do not differ materially from those previously calculated. The zero-correction for the constant-volume thermometer may be put in the form

$$\theta_0 - T_0 = 3.73 (c_0 - c_1) p_0 / R.$$

Taking  $c_0 = 1.48$  c. c., this gives  $0.72$  for the correction at 76 cms., or  $0.95$  at 100 cms. If we assume the correction for nitrogen to be the same as that for air, and employ Chappuis' pressure-coefficient, we find  $\theta_0 = 273.06$ . The values of the scale-correction for the air-thermometer are as follows at  $50^\circ$  C. and  $450^\circ$  C.:—

Constant-Pressure, 76 cms.

at  $50^\circ$  C.,  $dt = -0.185^\circ$ ; at  $450^\circ$  C.,  $dt = +.470^\circ$ .

Constant-Volume,  $p_0 = 76$  cms.

at  $50^\circ$  C.,  $dt = -0.044^\circ$ ; at  $450^\circ$  C.,  $dt = +.136^\circ$ .

Constant-Volume,  $p_0 = 100$  cms.

at  $50^\circ$  C.,  $dt = -0.057^\circ$ ; at  $450^\circ$  C.,  $dt = +.179^\circ$ .

The constant-pressure correction is nearly one-tenth larger, the constant-volume correction is nearly one-third smaller than in Table V., according to the previous method of calculation with  $n=2$ . The constant-volume correction is still nearly twice as large as that given by the Rose-Innes formula for nitrogen, and more than three times as large as that given by his formula for air. For nitrogen, if we simply adopt the values of the constants given for air, we find that they satisfy the observations of the compressibility at low temperatures, and of the pressure-coefficient ( $0^\circ - 100^\circ$  C.) rather better than those given by Rose-Innes, which depend on the very doubtful observations of the cooling-effect.

*Nitrogen.*—Although we should probably be well within the limits of experimental error in taking the corrections for nitrogen to be the same as those for air, I have thought it

worth while to calculate the values of the constants for nitrogen from Chappuis' pressure-coefficient at 100 cms., assuming  $\theta_0 = 273^\circ \cdot 10$ . This gives  $c_0 = 1.58$  c.c. Whence if  $c-b$  at  $0^\circ \text{C.} = 0.44$  c.c., we have  $b = 1.14$  c.c. Chappuis' observations of the compressibility at  $0^\circ \text{C.}$  give  $c_0 - b = 0.35$  c.c., which would make  $b = 1.23$  c.c. The volume of the liquid at its boiling-point is 1.26 c.c., but this is probably too large, so I have taken  $b = 1.14$ . The corrections calculated with these values are seen to be practically the same as for air.

*Hydrogen.*—In calculating the values of the constants for hydrogen on the assumption  $n = 1.5$ , I have taken Chappuis' value of the slope of the isothermals at  $0^\circ \text{C.}$ , namely,  $c_0 - b = -6.5$  c.c., which is in close agreement with Regnault's values, 5.5 to 6.6 c.c. at  $4^\circ \text{C.}$  Adopting also Joule and Thomson's value of the heating-effect at  $0^\circ \text{C.}$ , namely  $Q_0 = .0293^\circ$  per atmo, we have  $c_0 = 1.50$  c.c.,  $b = 8.0$  c.c. The value of  $b$  is slightly smaller than Amagat's limiting volume 8.7 c.c. at high pressures, and much smaller than the volume of the liquid 14 c.c., but it appears that hydrogen is much more compressible than other gases or liquids under these conditions.

TABLE XII.

Values of Constants assumed for Diatomic Gases.

Gas employed.	$c_0$ . c. c.	$b$ . c. c.	$c_0 - b$ . c. c.	$R$ $\times 10^{-6}$ .	$S$ . $\times 10^{-6}$ .	Factor $c_0 p_0 / R$ .	
						76 cms.	100 cms.
Air .....	1.48	0.98	0.50	2.872	10.05	0.516	0.678
Nitrogen ...	1.58	1.14	0.44	2.966	10.38	0.540	0.710
Hydrogen ...	1.50	8.00	-6.50	41.5	145.3	0.0367	0.0482

The value of the Absolute Zero  $\theta_0 = 273^\circ \cdot 101$  is deduced from the pressure-coefficient of hydrogen, and the pressure- and expansion-coefficients of the other gases are deduced on the assumption  $\theta_0 = 273^\circ \cdot 10$ .



TABLE XIII.

Expansion- and Pressure-Coefficients of Diatomic Gases.

Gas employed.	Constant-Pressure. 76 cms.			Constant-Volume, $p_0=100$ cms.		
	$\theta_0 - T_0$ .	$T_0$ .	$1/T_0$ .	$\theta_0 - T_0$ .	$T_0$ .	$1/T_0$ .
Air .....	0.71	272.39	.0036709	0.96	272.14	.00367425
Nitrogen ...	0.70	272.40	.0036708	0.99	272.11	.00367466
Hydrogen ...	-.135	273.235	.00365985	+ .067	273.034	.00366254

Regnault's values of the expansion-coefficient for hydrogen at 76 cms. range from .0036642 to .0036586. Chappuis at 100 cms. finds .0036600 for hydrogen at constant pressure, and .0036726 to .0036735 for nitrogen, the calculated values being .0036593 and .0036737 respectively.

The values of the thermodynamical corrections for the diatomic gases are calculated by the following formulæ:—

Assuming  $n=1.5$ ,  $c=c_0(\theta_0/\theta)^{1.5}$ ,  $c_0-c_1=0.3738c_0$ .

Zero-Correction C. P.,

$$\theta_0 - T_0 = (c_0 - b + 2.73 \times .374 \times c_0) p_0/R.$$

Zero-Correction C. V.,

$$\theta_0 - T_0 = 3.73 \times .374 \times c_0 p_0/R.$$

Scale-Correction C. P.,

$$dt = (0.3738 t/100 - 1 + (\theta_0/\theta)^{1.5}) c_0 p_0/R.$$

Scale-Correction C. V.,

$$dt = (0.1445 t/100 - 1 + (\theta_0/\theta)^{0.5}) c_0 p_0/R.$$

The densities of oxygen and nitrogen at the boiling-point of oxygen at a pressure of 760 mm. have been directly determined by Dewar (Proc. Roy. Soc. lxi. p. 360) by the method of weighing. The resulting values of the specific volumes were:—Oxygen,  $v=225.8$  c.c. per gramme, Nitrogen,  $v=256.8$  c.c. at  $90^\circ.5$  Abs. with a possible error of 0.5 per cent. The ideal volumes at this temperature and pressure are:—Oxygen, 231.8 c.c., Nitrogen, 264.9 c.c. The values of  $c-b$  at  $90^\circ.5$  Abs. are: Oxygen,  $c-b=6.0$  c.c.; Nitrogen,

2 A 2

TABLE XIV.

Scale-Correction for Diatomic Gases.

Temp. cent.	Constant-Pressure, 76 cms.			Constant-Volume, $p_0=100$ cms.		
	Air.	Nitrogen.	Hydrogen.	Air.	Nitrogen.	Hydrogen.
- 250	...	...	+1.43	...	...	+1.005
- 200	...	...	+ .201	+ .438	+ .460	+ .0311
- 150	+ .901	+ .945	+ .064	+ .186	+ .195	+ .0132
- 100	+ .314	+ .328	+ .0223	+ .076	+ .080	+ .0054
- 50	+ .086	+ .090	+ .0062	+ .0232	+ .0243	+ .00164
- 20	+ .0238	+ .0250	+ .00170	+ .0067	+ .0070	+ .00048
- 10	+ .0105	+ .0110	+ .00075	+ .0030	+ .0032	+ .00021
+ 10	- .0078	- .0082	- .00055	- .0023	- .0024	- .00016
+ 20	- .0134	- .0141	- .00095	- .0041	- .0043	- .00023
+ 30	- .0169	- .0177	- .00120	- .0051	- .0053	- .00036
+ 40	- .0186	- .0195	- .00132	- .0056	- .0059	- .00040
+ 50	- .0186	- .0195	- .00132	- .0056	- .0059	- .00040
+ 60	- .0172	- .0180	- .00123	- .0053	- .0054	- .00038
+ 70	- .0146	- .0153	- .00104	- .0046	- .0048	- .00032
+ 80	- .0106	- .0113	- .00077	- .0034	- .0036	- .00024
+ 90	- .0058	- .0061	- .00041	- .0019	- .0020	- .00013
+ 150	+ .0409	+ .0428	+ .0029	+ .0136	+ .0143	+ .00097
+ 200	+ .096	+ .101	+ .0068	+ .0332	+ .0347	+ .00236
+ 300	+ .232	+ .243	+ .0165	+ .084	+ .088	+ .0059
+ 450	+ .472	+ .495	+ .0336	+ .180	+ .189	+ .0127
+ 1000	+ 1.464	+ 1.535	+ .1040	+ .616	+ .646	+ .0438

$c-b=8.1$  c.c. Whence the value for air would probably be,  $c-b=7.7$  c.c. The calculated values at this temperature, on the hypothesis  $n=1.5$ , would be 6.8 and 7.2 c.c. for air and nitrogen respectively, which are probably within the limits of experimental error. If we assumed Dewar's values of  $c-b$  at  $90^{\circ}5$  Abs., and calculated the values of  $c_0$  at  $0^{\circ}$  C. on the assumption  $n=2$ , we should find for nitrogen  $c_0=0.95$  c.c.,  $b=0.51$  c.c., which do not agree so well with the values of the cooling-effect or with Chappuis' values of the coefficients.

The temperature of inversion of the heating-effect in the case of hydrogen has been observed by Olzewski to be about  $-80^{\circ}$  C., when the gas is supplied at a pressure of 117 atmos and escapes at atmospheric pressure. The values of the

constants above given on either assumption  $n=1.5$  or  $n=2$ , would give a small heating-effect  $SQ = -1.7$  c. c. at this point. But as the effect amounts to little more than a hundredth of a degree per atmo it would be easily masked by any slight impurity in the hydrogen, so that little stress can be laid on this observation. Assuming that the heating-effect  $Q$  is constant up to a pressure of 117 atmos, the observations of Olzewski would require  $c_0 = 2.0$  c. c.,  $b = 8.5$  c. c. if we take  $n=1.5$ , and  $c_0 - b = -6.5$  c. c. These values would make the heating-effect at  $0^\circ \text{C}$ .  $Q = -0.24^\circ$  per atmo, which is rather smaller than that observed by Joule and Thomson, but the difference is hardly beyond the possible limits of error. The absolute zero-correction for the constant-volume thermometer would be larger in the proportion of 2 to 1.5, but that of the constant-pressure thermometer would be smaller, agreeing slightly better with experiment. The value of  $c_0$  for hydrogen probably lies between 1 and 2 c. c., but we can hardly expect to be able to determine it more closely with certainty, since it is of the order of one part in 10,000 only of the specific volume at  $0^\circ \text{C}$ . and 760 mm. pressure.

### 21. *Summary of Conclusions.*

(1) The deviations of a gas or vapour from the ideal state at moderate pressures can be represented by an equation of the type  $v - b = R\theta/p - c$ , in which the "covolume"  $b$  is constant, and the "co-aggregation-volume"  $c$  is a function of the temperature only. This conclusion follows from the observed form of the isothermals combined with the observation that the "cooling-effect" is independent of the pressure; but it could not be deduced from either observation separately.

(2) The value of the Absolute Zero may be approximately deduced from a knowledge of the cooling-effect  $Q$  and the specific heat  $S$  at or near  $50^\circ \text{C}$ . without any knowledge of the mode of variation of  $S$  and  $Q$  with temperature. But the determination of the scale-correction of the gas-thermometer essentially requires a knowledge of the mode of variation with temperature.

(3) The simplest assumption with regard to the mode of variation of  $c$  with temperature is that it varies inversely as the  $n$ th power of  $\theta$ , or that  $c = c_0(\theta_0/\theta)^n$ . The value of  $n$  is

different for different types of co-aggregation or for different kinds of molecules. The law of Corresponding States must be restricted to molecules of the same type which coaggregate in a similar manner.

(4) The index  $n$  may be interpreted as half the number of degrees of freedom lost by a molecule in coaggregation, the energy of flight of a molecule representing three degrees of freedom.

(5) The value of  $n$  is probably 0.5 for monatomic gases, and 1.5 for diatomic gases, on the simple hypothesis of integral degrees of freedom. These values give very fair agreement with experiment, but there is no *a priori* reason why the number of degrees of freedom should be an integer for a polyatomic molecule.

(6) The properties of  $\text{CO}_2$  at moderate pressures are well represented by the assumption  $n=2$ , provided that account is taken of the variation of the specific heat as observed by Regnault. This reconciles the hitherto discordant results for the cooling-effect and the compressibility.

(7) The properties of Steam, including the variation of the latent heat and the saturation-pressure, are well represented by the value  $n=3.3$ , if the limiting value of the specific heat at zero pressure is assumed to be independent of the temperature, provided that the variation with pressure is not neglected.

(8) The value of the Absolute Zero, as deduced from the pressure-coefficient of hydrogen, is probably within one or two hundredths of a degree of  $273^{\circ}10$ .

#### DISCUSSION.

Prof. HERSCHELL asked whether the co-volume came into the correction.

Dr. HARKER looked forward to the experiments which Prof. Callendar proposes to make with a constant-pressure thermometer.

Dr. GLAZEBROOK expressed his interest in the extreme delicacy of the observations of Chappuis.

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XXVIII. *The Size of Atoms.* By H. V. RIDOUT.\*

[Abstract.]

THIS investigation is an outcome of the dissociation theory of electrolysis, with measurements directly derived from established electrical formulæ, and relates to a dissociated atom, as constituting *the smallest quantity of matter which can take part in an electrolytic action.*

As such it is only a fraction of the "atom" or "molecule" chosen by Loschmidt † and Lord Kelvin ‡ in their respective investigations.

The method consists in finding a pair of spheres, which would be charged by the quantity of electricity known to be necessary to electrolyse a given quantity of the body under examination—in this case water—to the known difference of potential of its ions, and from this equality the size of the ions, and hence the atoms, is directly arrived at.

114½ millions of hydrogen atoms to the linear centimetre is the number now found.

It is assumed :

- a. The dissociation theory is true.
- b. The atoms are spherical.
- c. Undissociated water has twice the dielectric capacity of space.
- d. The ions of water are HO and H.
- e. The component particles of water are in contact.
- f. The  $\pm$  ions occupy equal volumes.

The gram-ion is taken at 96,500 coulombs, and the potential difference of the ions at 1.5 as a round number.

Of these points, *a* is a condition precedent ; *b* is taken for simplicity ; *c* is taken as a round number approximating to the Clerk-Maxwell relation of capacity to refractive index §.

*d* : these are generally adopted in the dissociation theory.

\* Read October 31, 1902.

† *Sitzungsberichte der Wiener Akademie*, 1865, vol. iii. p. 881.

‡ *Nature*, 1883, p. 203 *et seq.*

§ In support of this see Blondlot, *Comptes Rendus*, 1894, vol. cxix. p. 595, and C. Gutton, *ibid.* 1900, vol. cxxx. p. 1119.

*e*: this must hold good, till it can be shown that water in some state has a greater density than water as we know it.

*f*: this appears to be the relation accepted in the dissociation theory. It is only adopted here to save discussion.

Taking  $O=16$ ;  $H=1$ ;  $1/9 \times 96,500=10,722$  coulombs are required for the electrolysis of 1 c.c. water. One coulomb will charge to 1 volt a sphere (isolated in space) of  $18 \times 10^{11}$  cm. diameter. But since the potential of the ions is taken at  $\pm 75$  volt, and the dielectric capacity of the surrounding undissociated water at 2; this gives

$$18 \times 10^{11} \times 10,722/2 \times 75 = 13 \times 10^{15} \text{ cm.}$$

as the diameter of the sphere, placed under the conditions of a solitary ion, required to hold the  $\pm$  electricity concerned in the decomposition of 1 c.c. water.

As the method involves a linear measurement, it will be convenient to regard the atoms as arranged in vertical columns. With this disposition, spheres, whatever the number required to fill a given tube, will have the same total volume as a single inscribed sphere. This relation holds true for all regular solids and their circumscribing figures. For the alternative disposition—or piled-shot arrangement of the atoms—the measurement found may be readily adapted.

The electrical capacities of spheres, under like conditions, being proportional to their diameters, it follows that the capacity of isolated spheres is equal to that of an isolated sphere of which the diameter is equal to the sum of the diameters of the spheres.

For the purpose of this investigation it will be convenient to take 2 one-centimetre cubes. Here the H ions weigh  $1/9$  gram. If we suppose the water to be completely dissociated into ions, the actual volume of the hydrogen ions will be represented by a sphere of 1 cm. diameter, and, as shown, this carries a quantity of electricity which would charge a sphere of  $13 \times 10^{15}$  cm., placed under like conditions. But this quantity will also charge  $13 \times 10^{15}$  spheres, each of 1 cm. diameter; further, the same reasoning may be applied to each 1 cm. sphere, and we get as a result, an equal number of columns, each 1 cm. high, and thus the question for solution is, what must be the thickness of the 1 cm. high columns,

so that  $13 \times 10^{15}$  may be packed in the 1 cm. cube? The number of columns side by side to measure 1 cm. equals the square root of the number to be packed, but this equals also the number of spheres in each 1 cm. column =  $114\frac{1}{2}$  millions approximately.

The dissociation theory requires that the ions shall be beyond the range of each other's influence. It is singularly in accord with all observation, that a current of infinitesimal electromotive force can decompose an electrolyte, whatever the difference of potential of its ions. It is also found that the amount of decomposition with a given quantity of current is the same, whatever the concentration of the electrolyte, and therefore the relative approximation of the ions. Such facts are consistent with isolation alone: and once this is proved, the self-repulsiveness of the elements of a charge ensures the symmetrical distribution of the charge about its sphere.

It may appear that our sphere of  $13 \times 10^{15}$  cm. fixes only the superior limit of size of the atom in the case considered; but in reality it fixes both the limits. It is the *smallest* sphere which can hold the given quantity of electricity at the given potential, and can therefore be subdivided into the *fewest* spheres which can at once hold the given charge, and fill the given cube. Thus it fixes the *superior* limit of size of the atom. Further, it is the *largest* sphere which can be charged to the given potential with the given quantity of electricity, and this, for like reason, fixes the *inferior* limit of size of the atom. Thus, under the given conditions,  $114\frac{1}{2}$  millions per linear centimetre expresses both the limits, and is therefore the true value.

#### DISCUSSION.

LORD KELVIN remarked that he had often concerned himself with the size of atoms, and pointed out that the value obtained by the Author for the diameter of a hydrogen ion was almost exactly one half of that which he had obtained for the diameter of a molecule of hydrogen. The fact, however, might be a coincidence. He had dealt with a sphere, which would have the same effect as a double atom of hydrogen. While avoiding the assumption that atoms are

hard and spherical, it was usual to treat them as such for purposes of calculation. The paper was an important one, but there were many assumptions which required looking into. Lord Kelvin said that in dealing with the subject of atoms, it was necessary to consider the atoms of electricity. The atomic theory of electricity, now almost universally accepted, had been thought of by Faraday and Clerk-Maxwell and definitely proposed by Helmholtz. The atoms of electricity were very much smaller than the atoms of matter, and permeated freely through the spaces occupied by these greater atoms and also freely through space not occupied by them. An atom of electricity in the interior of an atom of matter experienced electric force towards the centre of the atom. We were forced to conclude that every kind of matter had electricity in it, and Lorenz had named electricity as the moving thing in atomic vibrations. If the electrions, or atoms of electricity, succeeded in getting out of the atom of matter, they proceeded with velocities which may exceed the velocity of light, and the body was radioactive. It was therefore not surprising that some bodies showed radioactive properties, but rather surprising that such properties were not shown by all forms of matter. Our knowledge of this subject, which originated with the discovery of the Becquerel rays, had been greatly advanced by the experiments carried out at the Cavendish Laboratory, and he had no doubt that in the next two or three years much light would be thrown upon this important matter.

Prof. EVERETT said the author had taken the specific inductive capacity of water as 2, whereas experimenters had found it to be about 80.

The AUTHOR, in replying, said the value found for ice was about 2.

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XXIX. *On the Existence of a Relationship between the Spectra of some Elements and the Squares of their Atomic Weights.*  
By W. MARSHALL WATTS, D.Sc., F.I.C.\*

It is well known that the spectra of some allied elements exhibit certain resemblances; so that in the spectrum of one element we have, as it were, the spectrum of another shifted through a certain distance. This has been made clearer by the resolution of the lines of certain spectra into groups by Kayser and Runge, who have shown that in many cases the wave-lengths of the lines of a spectrum can be calculated with considerable accuracy by means of a formula based upon that applied with such striking success by Balmer to the spectrum of hydrogen. In a general way it may be said that an increase in atomic weight produces a shift towards the red end of the spectrum, and the amount of the shift seems in many cases to admit of simple expression in terms of the squares of the atomic weights.

There appear to be two distinct kinds of connexion between the spectra of allied elements. In one class of cases, of which the family of zinc, cadmium, mercury, and that of gallium and indium furnish the best examples, the differences between the oscillation-frequencies of certain lines of the one element are to the differences between the oscillation-frequencies of the corresponding lines of the other element as the squares of their atomic weights; so that, if it be admitted that the lines *do* correspond, it is possible to calculate the atomic weight of the one element from that of the other by means of the spectra.

In the other class of cases, of which the families potassium, rubidium, and caesium, and calcium, strontium, and barium offer the best examples, the element of greater atomic weight has the smaller oscillation-frequency, and three elements are so related that the differences of oscillation-frequency between the elements, in comparing corresponding lines in their spectra, are proportional to the differences between the squares of the

\* Read October 31, 1902.

atomic weights; so that we can calculate the atomic weight of one element from the atomic weights of two other elements of the same family by means of their spectra.

In the spectra of lithium, sodium, potassium, rubidium, and caesium Kayser and Runge distinguish a principal series and two secondary series, the lines of each series being connected together by a formula of the form

$$\frac{1}{\lambda} = A[1 - Bn^{-2} - Cn^{-4}],$$

where A, B, C are constants, and  $n$  receives the values 1, 2, 3, 4, &c.

The lines in each series, therefore, approach closer and closer together towards the violet, coming to a limit at the oscillation-frequency given by the value of A, which is termed the convergence-frequency. The values of the constants for the principal series of the elements named are:—

	A.	B.	C.
Lithium .....	43584.73	3.06688	25.24012
Sodium .....	41536.81	3.12939	19.33950
Potassium .....	35066.55	3.61914	17.82216
Rubidium .....	33762.11	3.71781	16.65343
Cæsium .....	31501.56	3.97050	15.55107

Here the differences of convergence-frequency of potassium rubidium, and caesium are nearly proportional to the differences in the squares of the atomic weights; but the same does not hold between lithium, sodium, and potassium. The convergence-frequency of sodium, calculated from those of lithium and potassium on this hypothesis, would be about 40810.

The two rules stated above are probably only approximations to the truth—the results of the calculations made would agree more closely with the known values if the actual law were not more complicated than that assumed.

The numbers given below will show what amount of accuracy may be expected.

*Example 1.* From the atomic weight of cadmium, 111·83, to calculate that of zinc (64·9).

The following are the oscillation-frequencies of the lines assumed to correspond:—

	Cadmium.		Zinc.
(a)	30654·4 10r		32500·0 8r
(b)	30734·9 8b		32540·1 10r
(c)	31905·5 8b		32928·7 10b
(d)	32446·8 6b		33118·6 8b
(e)	36023·7 6b		34310·8 4
(f)	37334·5 8		34791·3 6
(g)	38851·1 4		35285·7 8r
(h)	39280·5 2n		35408·9 6
(i)	43690·5 10r		36934·7 6
(j)	44086·7 4r		37059·2 2b
(k)	44630·0 6r		37242·2 8b
(l)	45550·6 1		37548·1 8

From these numbers we get for the atomic weight of zinc by combining—

(a) & (c)	65·44
(a) & (d)	65·09
(a) & (f)	65·48
(a) & (g)	65·17
(a) & (h)	64·93
(a) & (i)	65·28
(a) & (j)	65·15
(a) & (k)	65·12
(a) & (l)	65·16
(b) & (e)	64·69
(c) & (e)	64·77 and so on.

	Cadmium.		Zinc.
(m)	19655·8 10r		21170·0 10r
(n)	20826·7 10r		21591·6 8b
(o)	28840·2 10r		24371·4 2
(p)	30301·9 4		24869·7 4

(m) & (n)	67·08
(n) & (o)	65·38
(n) & (p)	65·76
(m) & (p)	65·98

	Cadmium.		Zinc.
(q)	27669·1 8r		29885·1 10r
(r)	29370·4 10r		30456·0 8r

(q) & (r) give 64·78 for the atomic weight of zinc.

*Example 2.* From the atomic weight of mercury, 199·71, to calculate the atomic weights of cadmium and zinc.

The following are the lines assumed to correspond :—

	Mercury.		Cadmium.		Zinc.	
(a)	16250	10	.....		21359.5	10 r
(b)	18368.4	10 r	20828.7	10 r	21591.6	8 b
(c)	20156.3	2 b	21368.7	10 r		
(d)	20334.0	6 b	21440.4	8 b		

(a) & (b) give 68.13 for zinc.

(b) & (d) give 111.45 for cadmium.

(b) & (c) give 109.59 for cadmium.

(e)	20334.0	6 b	27669.1	8 r	29835.1	10 r
(f)	24037.4	4 b	28840.2	10 r	30265.9	8 r
					30269.2	8 r
(g)	25578.2	1 n	29370.4	10 r	30456.0	8 r
(h)	29628.1	4 b	30654.4	10 r		
(i)	30245.9	1 b	30734.9	8 b		

(e) & (i) give 111.06 for cadmium.

(e) & (g) „ 113.7 for cadmium and 65.9 for zinc.

(e) & (f) „ 112.3

(e) & (h) „ 110.1

*Example 3.* From the atomic weight of indium, 113.7, to calculate that of gallium (69.9).

The following lines are assumed to correspond :—

	Indium.		Gallium.	
(a)	22159.3	10 r	23961.1	20 r
(b)	24371.8	8 r	24787.3	10 r

(a) & (b) give 69.47.

(c) 30701.5 10 r 33954.1 1 n

(d) 32890.5 10 r 34780.8 2 n

(c) & (d) give 69.87.

*Example 4.* From the atomic weight of barium, 136.76, and that of calcium, 39.99, to calculate the atomic weight of strontium (87.37).

The lines assumed to correspond are :—

	Barium.		Strontium.		Calcium.	
(a)	15387	6 r	19388	10	21617	1 b
(b)	17873	4 n	22061	6	24390	4 b
(c)	21951	10 r	26976	6 n	29736	8 b
(d)	22979	8 r	28177	6 n	30991	4 b
(e)	24201	8 r	29399	1 n	32229	1 n

From (a) we get 87.85 for the atomic weight of strontium.

(b) 87.82

(c) 87.54

(d) 87.22

(e) 87.34

*Example 5.* From the atomic weight of caesium, 132·7, and that of potassium to calculate the atomic weight of rubidium (85·2).

The following lines are assumed to correspond :—

	Caesium.		Rubidium.		Potassium.
(a)	12469 6		13742 4		14465 7
(b)	21784 6r		23714 6r		24700 6r
(c)	21945 8r		23791 8r		24719 8r
(d)	25707 4r		27833 4r		28998 6r
(e)	25787 6r		27868 6r		29006 8r
(f)	27638 2r		29832 2r		31068 4r
(g)	27678 4r		29852 4r		31073 6r
		(a) gives	86·87		
		(b)	83·24		
		(c)	83·11		
		(d)	84·51		
		(e)	84·93		
		(f)	85·52		
		(g)	85·51		

And the convergence-frequencies 31502, 33762, and 35086 give 86·02.

Mitscherlich, so long ago as 1864, pointed out the similarity in the spectra of the chloride, bromide, and iodide of barium, and endeavoured to trace a connexion with the atomic weights of these compounds.

Lecoq de Boisbaudran in 1869 called attention to the spectra of the metals of the alkalies and alkaline earths, remarking that the spectrum of caesium is like that of potassium shifted bodily towards the red. Hartley in 1890 showed that three triplets in zinc corresponded with three triplets in cadmium, and that in each of these spectra the triplets had their lines similarly spaced if mapped on the scale of oscillation-frequency. Kayser and Runge in 1891 confirmed this statement, and point out many more triplets similarly related, for which they found a connecting formula of the form

$$\frac{1}{\lambda} = A(1 - Bn^{-2} - Cn^{-4}).$$

They further call attention to the fact that the differences in oscillation-frequency in the triplets increase with increase of atomic weight; and that they are nearly as the squares of the atomic weights. They also remark that in the spectra of

potassium, rubidium, and cæsium the mean differences of the close pairs are nearly proportional to the squares of the atomic weights.

Ramage (Proc. Roy. Soc. 1901) has discussed many of these relationships, and gives two diagrams with oscillation-frequencies as abscissæ, one with atomic weights as ordinates, the other with the squares of atomic weights as ordinates. He points out that in the second of these two diagrams, the lines connecting corresponding points are nearly straight in the case of potassium, rubidium, and cæsium; and in the case of calcium, strontium, and barium. He remarks also that "curious results were obtained by observing the points in which the converging lines, drawn through corresponding members of doublets and triplets, intersected. It was difficult to determine these points accurately, and the results have since been regarded more as coincidences."

In a more recent paper (June 5th, 1902) on the spectra of potassium, rubidium, and cæsium Ramage confirms his previous results, and says that the lines connecting corresponding members of homologous doublets do actually intersect on the line of zero atomic weight.

#### DISCUSSION.

Lord KELVIN expressed his interest in the paper.

Prof. PERRY asked to what extent the points actually lay upon straight lines. He had worked with the spectra of potassium, rubidium, and cæsium, and knew that many relations which apparently held, on careful examination were found not to be true on account of certain points falling slightly off the curves. He would like to compare the Author's results with some of his own work.

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XXX. *On a Determination of the Ratio of the Specific Heats at Constant Pressure and at Constant Volume for Air and Steam.* By WALTER MAKOWER, B.Sc., University College, London\*.

[Plate IV.]

### 1. *Introduction and General Method.*

THE method employed was similar to that used by Lummer and Pringsheim (Smithsonian Contributions to Knowledge, 1898), which consists in allowing the gas under investigation to expand adiabatically and measuring the lowering of temperature caused by such expansion.

In these experiments the initial and final pressures of the gas were measured on a sulphuric-acid gauge, and the change of temperature deduced from the variation of the electrical resistance of a fine platinum-bolometer strip immersed in the gas under investigation. The gases experimented upon were air, oxygen, carbon dioxide, and hydrogen, for which the values of the ratio of the two specific heats were found to be 1.4025, 1.3977, 1.2995, 1.4084 respectively.

The chief modifications introduced in the present investigation consist in the substitution of a platinum-thermometer with compensating leads, for the bolometer-strip of Lummer and Pringsheim, who employed a somewhat different device for eliminating errors due to conduction of heat along the leads. Also, at the suggestion of Prof. Callendar, the electrical contacts were made by means of a specially constructed automatic mercury switch, instead of by hand. It was also hoped that it might be possible to use smaller quantities of gas than Lummer and Pringsheim had used, and it was partly with the object of testing this point that the present investigation was undertaken.

If  $\theta_1$  and  $\theta_2$  be the initial and final temperatures of the gas, and  $p_1$  and  $p_2$  the initial and final pressures respectively,

\* Read November 14, 1902.

then according to the well-known relation

$$\gamma = \frac{\log(p_1/p_2)}{\log(p_1/p_2) - \log(\theta_1/\theta_2)} \cdot \cdot \cdot \cdot \cdot \quad (1)$$

If then the gas be allowed to expand in such a manner that  $p_1$ ,  $p_2$ ,  $\theta_1$  and  $\theta_2$  can be measured, the ratio ( $\gamma$ ) of the specific heat at constant pressure to the specific heat at constant volume can be calculated.

In the case of steam, which could not be considered as a perfect gas at the temperatures at which the present experiments were made, the characteristic equation proposed by Callendar (Proc. R. S. lxvii. 1900) was employed. On this assumption the adiabatic relation is still given by equation (1).

## PART I.

### 2. *Experiments with Air.*

The apparatus employed is shown on Plate IV. It consisted of a large spherical copper vessel (not shown in the figure) which we will call the "air-vessel," of about 50 litres capacity, connected to a tube C for admitting the air to be experimented with; into the "air-vessel" passed a platinum thermometer by means of which the fall of temperature on expansion of the air at a point near the centre of the vessel was measured. Into the neck of the vessel was soldered a side tube of 1.8 cm. diameter. By withdrawing a rubber stopper (*b*) fitting tightly into this tube the pressure in the vessel was allowed to fall from a value ( $p_1$ ) previously adjusted to the atmospheric pressure ( $p_2$ ). By means of the tube D the "air-vessel" was connected to an oil manometer M which could be placed in communication with the experimental vessel or cut off from it at will by means of the glass tap E. The usual arrangement for measuring the resistance of the platinum thermometer is also shown in the figure. In connexion with the "air-vessel" was a mercury-gauge N which served as an automatic key for closing the battery-circuit at a definite instant after releasing the pressure of the air. The gauge N was connected by rubber *r* to a T-piece in the tube D, through which passed a platinum wire *w*, just dipping into the mercury when the pressure inside the apparatus was equal to the pressure of



the atmosphere. Dipping into the other arm of the gauge was a wire  $x$  passing out through a loosely fitting cork  $c$ , through which also passed a glass tube with a platinum wire  $p$  sealed through it, electrically connected to  $w$ . (This was employed in the chronograph measurements to be described below.) When the pressure in the "air-vessel" was equal to the atmospheric pressure, the wire  $w$  was in electrical connexion with the wire  $x$ ; on raising the pressure the contact between the wire  $w$  and the mercury was broken, thus breaking the electric circuit from the wire  $w$  through the mercury to the wire  $x$ . If the pressure in the "air-vessel" was now suddenly released, contact was made between the mercury and the wire  $w$  after a definite time had elapsed. This time (which we will denote by  $\tau$ ) could be varied at will by raising or lowering the limb containing the wire  $x$ , and also by means of a screw pinch-cock (not shown in the figure) which served to constrict, to a greater or less extent, the rubber tubing joining the two limbs of the gauge. The two wires  $x$  and  $w$  were connected respectively to the two terminals of the key  $K$ , thus putting the gauge in parallel with this key.

### 3. *Measurement of Temperature.*

From formula (1) it appears that it is necessary to measure both the temperature ( $\theta_1$ ) before opening the vessel and the temperature ( $\theta_2$ ) to which the gas has fallen, measured at an instant as soon as possible after opening the vessel, as the gas begins to heat up, by conduction from the walls of the vessel, almost at once after releasing the pressure. In order, therefore, to obtain reliable results it is necessary that the thermometer which is used should be able to follow as nearly as possible the variations of temperature of the gas. On this account a platinum thermometer of a pattern similar to that employed by Callendar in his steam-engine experiments of 1895 was constructed.

A piece of pure platinum wire ( $p$ ) (Pl. IV. fig. 2) of diameter .001 inch was soldered \* on to the platinum leads  $l$  sealed

\* In the air-experiments ordinary soft solder was used. In the steam experiments to be described below the fine platinum wires were attached with silver solder.

through one end of the glass tubes  $g$ ; these in turn were soldered on to the copper leads  $L$ , passing out of the glass tubes through the other ends which were left open. Close to the thermometer leads were placed compensating leads to which were soldered a piece of fine platinum wire  $p'$  of the same diameter as the thermometer wire, but of shorter length, sufficiently long, however, to eliminate any end-effect error due to conduction of heat from the stout platinum leads to the fine platinum-thermometer wire. The four glass tubes were placed closely side by side, and introduced into the "air-vessel" through a stopper. To measure the resistance of the thermometer, the thermometer and compensating leads were connected to the two arms of the Wheatstone-bridge, as shown in figure 1. In order to keep the heating effect in the thermometer, due to the passage of the electric current, below  $0.01^{\circ}\text{C}$ . the current used in the resistance measurements was made sufficiently small, being supplied by one Leclanché-cell through 240 ohms in the battery-arm. The resistances of the two ratio arms were 3 ohms each. To obtain the balance position, a Thomson galvanometer was used, which, however, was rendered astatic to avoid unsteadiness caused by magnetic disturbances.

In all resistance measurements the galvanometer circuit was kept permanently closed, the battery circuit being broken or made by means of the keys. In this way trouble due to thermoelectric E.M.F.'s was avoided.

*Measurement of  $\theta_1$ .*—Air was pumped into the "air-vessel" until the pressure inside exceeded that of the atmosphere by a definite amount (about 67 cms. of oil), time being allowed for the air to assume a constant temperature. The resistance of the thermometer was read off by adjusting the resistance  $R$  and the sliding contact  $s$  with sufficient accuracy to give the temperature of the thermometer to  $0.01^{\circ}\text{C}$ . The battery circuit was closed by hand by means of the key  $K$ .

*Measurement of  $\theta_2$ .*—The resistance  $R$  was then diminished and the sliding-contact adjusted by judgment nearly to the position where there would be no current through the galvanometer at the instant when the battery circuit was made by means of the automatic gauge-key  $N$ . If the sliding-contact was adjusted exactly to the right position, the

galvanometer-needle remained at rest for an instant, and then gradually moved off as the thermometer heated up again. If, however, the shift was too small the needle gave a kick in the opposite direction to that corresponding to the heating up of the thermometer, came to rest, and then changed the direction of its motion, and gradually moved off as before as the gas heated up. In making the observations that position of the slider was sought for which the kick of the galvanometer just vanished.

To determine the time which elapsed between the instant of removing the stopper *b* and that at which the mercury in the gauge made contact with the wire *w*, the contact *e* was disconnected from *f* and connected to *g*, thus cutting out the Wheatstone-bridge and placing the gauge-key *N* in series with a storage-cell *S* and a chronograph. The platinum point *p*, which was electrically connected to *w*, was brought just into contact with the top of the mercury-column, when the air in the "air-vessel" was adjusted to the initial pressure ( $p_1$ ). On releasing the pressure the chronograph circuit was broken at *p* and made again through the wire *w*, after the expiration of a certain time (depending on the rate at which the mercury fell), which was measured on the chronograph to about .01 second.

This time was varied from .5 second up to about 5 seconds.

#### 4. *Pressure Measurements.*

The excess pressure ( $p_1 - p_2$ ) in the "air-vessel" before opening to the atmosphere was measured on a manometer *M* filled with Fleuss-pump oil. The density and coefficient of expansion having been carefully determined, the excess pressure could be obtained in centimetres of water by means of the formula

$$\text{density} = .8826 - .000644 t$$

(where  $t$  = temperature centigrade)\*.

As the oil used was exceedingly viscous some trouble was experienced at first, owing to the long time taken by the oil

\* The density and coefficient of expansion of the oil were determined by Mr. N. Eumorfopoulos, of University College, who very kindly supplied me with the oil used in these experiments.

in running down the sides of the tube when the pressure was altered. For this reason the position of the oil in the manometer was prevented from shifting more than two or three centimetres by closing the tap E immediately before opening the stopper *b*.

The pressure ( $p_2$ ) was obtained by reading the barometer.

### 5. Observations.

The following is a series of observations.

The resistances are given in arbitrary units, of which  $100 = 1.31$  ohms approximately.

The kicks of the galvanometer-needle are given in terms of the micrometer-divisions in the eyepiece of the reading microscope.

By plotting  $K$  against  $r$  the change of resistance corresponding to no kick of the galvanometer is found to be  $10.47$ .

TABLE I.

Resistance (R) before opening vessel.	Resistance (R) after opening vessel.	Kick of galvr. in micrometer divisions. K.	Change of Resistance $r$ .
651.00	640.54	no kick	10.46
651.19	640.84	3	10.35
651.27	641.04	5	10.23
651.38	641.24	10	10.14
651.61	641.44	10	10.17
651.62	651.34	5	10.28
651.82	641.49	4	10.33
651.97	641.54	2	10.43

Barometric pressure =  $767.6$  mm. mercury at  $0^\circ$  C.  
 =  $1044$  cms. of water at  $0^\circ$  C.

Excess pressure =  $67.1$  cms. oil at  $18^\circ$  C. =  $58.3$  cms. water.  
 The coefficient of the platinum wire used in the thermometer was  $.003835$  and its resistance at  $0^\circ$  C. was  $610.58$ . Hence  $2.34$  units of resistance correspond to  $1^\circ$  pt.; therefore a shift of  $10.47$  units corresponds to a change of temperature of  $4^\circ.48$  pt. =  $4^\circ.43$  C.

$$\therefore \gamma = \frac{\log \frac{1102.3}{1044}}{\log \frac{1102.3}{1044} - \log \frac{289.83}{285.4}} = 1.396.$$

For this experiment  $\tau = .76$  second.

### 6. Corrections and Results.

To the value of  $\gamma$  found above there are two corrections to be applied:—

(1) The air in the immediate neighbourhood of the thermometer has risen in temperature by conduction and convection during the time ( $\tau$ ) which elapses between opening the stopper  $b$  and closing the battery circuit.

(2) The final temperature as indicated by the thermometer will be higher than the temperature of the air surrounding it on account of direct radiation from the walls of the vessel.

(1) In order to find how much the air had heated up before the battery-circuit was closed by the automatic key, a number of observations were taken similar to those given above, but with different values of  $\tau$ . A series of values of  $\gamma$  was thus obtained for different values of  $\tau$ , from which it was possible to deduce the value  $\gamma$ , which would have been obtained had no time been allowed for the air round the thermometer to heat up. For since

$$\log \left( \frac{\theta_1}{\theta_2} \right) = \frac{\gamma-1}{\gamma} \log \left( \frac{p_1}{p_2} \right), \quad \dots \dots (2)$$

we see, by expanding by the logarithmic series and neglecting all terms except the first, that

$$(\theta_1 - \theta_2) = \theta_2 \frac{p_1 - p_2}{p_2} \frac{\gamma-1}{\gamma}. \quad \dots \text{(approximately)} (3)$$

Hence  $\frac{\gamma-1}{\gamma}$  is proportional to the fall of temperature.  $\frac{\gamma-1}{\gamma}$  as calculated from (2) was plotted against  $\tau$ , and by extrapolating back to  $\tau=0$  the value of  $\frac{\gamma-1}{\gamma}$  corresponding to no heating of the thermometer, due to conduction and convection, was obtained.

In Table II. are given the values obtained :—

TABLE II.

Time of closing circuit in seconds ( $\tau$ ).	$\gamma$ .	$\frac{\gamma-1}{\gamma}$ .
0.76	1.396	.2837
1.12	1.396	.2837
1.90	1.386	.2785
3.33	1.381	.2759
1.83	1.386	.2785
1.45	1.392	.2816
3.00	1.380	.2754
2.30	1.386	.2785
5.00	1.380	.2754
4.01	1.380	.2754
0.95	1.396	.2837
5.15	1.380	.2754
1.90	1.389	.2801
1.65	1.389	.2801
2.13	1.391	.2811
2.15	1.391	.2811

Assuming the variation of  $\frac{\gamma-1}{\gamma}$  with  $\tau$  to be linear over the small range considered, the value of  $\frac{\gamma-1}{\gamma}$  corresponding to  $\tau=0$  is .285. Hence  $\gamma=1.399$ .

(2) The error due to radiation was allowed for by coating the thermometer with platinum black. Assuming that the absorption by a platinum-blackened surface is 15 times as powerful as that of a bright surface\*, the error due to radiation could be estimated.

The value of  $\gamma$  obtained with a platinum-blackened thermometer was 1.360 for  $\tau=0.86$  second.

Since the value of  $\gamma$  corresponding to  $\tau=0.86$  sec. is 1.394, the correction to be applied for radiation is

$$\frac{1.394-1.360}{14} = .0024.$$

Hence the corrected value of the ratio of the two specific heats of air is  $\gamma=1.401$ .

\* Lummer and Pringsheim, *loc. cit.*

## PART II.

7. *Experiments with Steam.*

It will be readily understood that in order to determine the ratio of the two specific heats for steam, the use of vessels of the size employed in the experiments with air just described would be exceedingly inconvenient; and indeed the large size of the vessel does not seem to present the same advantage as in experiments made by the method of Clement Desormes. In the latter method the whole of the gas contained in the vessel is being experimented with, and consequently any error due to the heating of the gas close to the walls produces serious errors in the value of  $\gamma$  obtained; it is therefore desirable to reduce the surface of the vessel compared with its volume. In the present method, however, it is merely with the variation of temperature at the point where the thermometer is situated with which we are concerned, and any heating of gas near the walls of the vessel is unimportant. It therefore seemed likely that results of equal accuracy to those obtained with a large vessel might be obtained with a far smaller one.

To test this point experiments were made with air contained in smaller vessels, and the following apparatus was finally constructed for the steam experiments.

A cylindrical copper vessel with coned ends of about 9.3 litres capacity (Pl. IV. fig. 3) was constructed having a wide tap A, by opening which the steam could be allowed to expand adiabatically.

A tube D, provided with a tap through which the vessel could be filled with steam, passed through the lower extremity. On either side of the vessel tubes (B and C) were attached; through B a platinum thermometer was inserted; C communicated through a tap and a fine tube E with a glass tube which was connected to the oil manometer and automatic key. The whole was inclosed in a copper jacket filled with steam maintained at an excess pressure of about half an atmosphere, so that the steam in the inner vessel was superheated about  $10^{\circ}$  C.

The pressure in the jacket was kept constant by means of

an automatic gas-regulator devised by Callendar, which controlled the supply of coal-gas reaching the burner employed for heating the boiler which generated the steam. It was found that by this device the pressure could be kept constant to 1 mm. of mercury. To keep the temperature as constant as possible the whole vessel was packed in cotton-wool.

To prevent the condensation of steam in the tube E a small metal tap T was attached close to the vessel; this tap was not opened until the pressure in the vessel had become constant. By pumping in air the pressure in the tube E was raised slightly above that of the steam in the experimental vessel, so that on opening the tap T a small quantity of air passed into the vessel preventing steam from passing into the tube E and condensing there. In order to roughly determine the pressure of the steam before opening the tap T a small auxiliary mercury gauge was attached to C close to the vessel; when the pressure as registered by this gauge was constant, and had been adjusted to about the value required for taking an observation, the tap T was opened, thus putting the oil manometer in connexion with the vessel. As the tube E was fine very little steam diffused into it, and no trouble was experienced from this cause when the experiment was carried out as described. To get rid of any small quantity of moisture which might collect after the apparatus had been working for several hours, a T-piece F provided with a drain-tap was attached through which such moisture could be expelled. To carry out an experiment, the jacket was filled with steam under pressure, the tap A being open, and the tap D was then opened and steam allowed to enter the vessel, until all the air had been expelled; the taps D and A were then closed. It was found that the pressure in the vessel rose for a short time on account of a small quantity of water carried over by the steam entering through D. The pressure of the steam was then adjusted to a suitable value (about 56 cms. of water above the atmospheric pressure) and allowed to become constant. The tap T was then opened, after which the tap A was quickly opened and the pressures and temperatures registered, as in the experiments with air. The initial temperature ( $\theta_1$ ) was always observed just before opening the



tap A, only a few seconds being allowed to elapse between taking this observation and opening the tap. Temperatures were read to  $\cdot 02^{\circ}$  C. and pressures to the nearest millimetre of oil.

Before proceeding to a discussion of the results obtained for steam, the values of  $\gamma$  obtained for air, using the same apparatus, are given as an indication of its sensitiveness.

TABLE III.

Time of closing the circuit in seconds ( $\tau$ ).	$\gamma$ .
0.58	1.397
1.21	1.392
2.00	1.392

The value obtained with a platinum-blackened thermometer was 1.374; the correction to be applied for radiation is therefore  $\cdot 0017$ ,

$$\therefore \gamma = 1.399.$$

The striking agreement of this value with that obtained with the large vessel demonstrates conclusively that it is possible by the method here employed to work with quantities of gas far smaller than has hitherto been supposed.

#### 8. Observations and Results.

The observations were taken in a manner similar to that adopted in the case of air; it was, however, found inconvenient to take all observations between exactly the same pressure limits. The excess pressure was therefore adjusted approximately to the same value in each experiment, and, as in the air-experiments, the sliding-contact was adjusted by judgment *nearly* to the position where there would be no current through the galvanometer at the instant when the battery-circuit was closed; from the initial and final temperatures and pressures a value of  $\frac{\gamma-1}{\gamma}$  was calculated, which, as has been shown above, is proportional to the fall of temperature for a constant excess pressure. The kicks of the

galvanometer-needle were recorded and a correction applied to the value of  $\frac{\gamma-1}{\gamma}$  obtained, in order to allow for the fact that the sliding-contact had not been *exactly* adjusted to the correct position.

In the first series of observations a kick of 1 scale-division corresponded to  $\cdot 0012$  on  $\frac{\gamma-1}{\gamma}$ ; in the second series of observations a kick of 1 scale-division corresponded to  $\cdot 0016$  on  $\frac{\gamma-1}{\gamma}$ . The observations are given in full below.

TABLE IV.—Series I.

$\theta_1$	$\theta_2$	$P_1$ in cm. water at 0° C.	$P_2$ in cm. water at 0° C.	Kick of galvanometer in scale- divisions.	$\frac{\gamma-1}{\gamma}$ uncorrected for kick of galv.	$\frac{\gamma-1}{\gamma}$ corrected.
383-30	379-02	1081-2	1028-0	9	·2250	·2358
383-30	378-50	1084-6	1028-0	3	·2349	·2385
383-20	378-37	1084-0	1028-0	no kick	·2395	—
383-50	378-86	1085-4	1030-0	2	·2325	·2349
383-40	378-79	1094-5	1036-0	10	·2200	·2320
383-40	378-69	1091-6	1036-0	no kick	·2367	—
383-40	378-63	1093-5	1036-0	3 or 4	·2314	·2356
383-30	378-53	1092-7	1036-0	no kick	·2349	—
383-30	378-61	1091-6	1036-0	1 or 2	·2355	·2373
383-30	378-79	1090-9	1036-0	3	·2284	·2320
383-30	378-76	1088-4	1035-0	1	·2372	·2384
383-30	378-87	1087-9	1035-0	3	·2331	·2367
383-30	378-83	1090-7	1035-0	17	·2243	·2147
383-30	378-79	1090-4	1035-0	4	·2272	·2320
383-20	378-99	1086-0	1035-0	3	·2296	·2332
383-20	379-02	1086-9	1035-0	2	·2248	·2372
383-20	378-93	1091-0	1035-0	17	·2157	·2361
383-20	378-93	1087-2	1035-0	just a kick	·2308	·2308
383-40	378-82	1090-7	1035-0	7	·2296	·2380
383-40	378-72	1090-3	1035-0	2	·2355	·2379
383-30	378-67	1090-5	1035-0	2 or 3	·2326	·2356
383-10	378-83	1075-8	1021-0	10	·2145	·2265
383-00	378-64	1075-2	1021-0	2	·2212	·2236
383-00	378-46	1077-1	1021-0	5	·2230	·2290
383-00	378-29	1077-7	1021-0	1	·2290	·2302
383-00	378-25	1073-0	1017-0	2	·2331	·2355
383-00	378-21	1073-4	1017-0	1	·2331	·2343
382-90	378-21	1069-4	1015-0	3	·2367	·2403
382-70	377-89	1066-0	1009-0	3 or 4	·2302	·2344
382-70	377-89	1063-8	1009-0	2	·2390	·2414
382-90	378-03	1073-8	1018-0	no kick	·2401	—
383-10	378-23	1076-9	1021-0	no kick	·2395	—
383-40	378-42	1091-2	1035-0	no kick	·2401	—
383-40	378-51	1090-9	1035-0	no kick	·2441	—

For these observations  $\tau = 0.67$  second.

Mean value of  $\frac{\gamma-1}{\gamma} = .2349$ ,

whence  $\gamma = 1.307$ .

TABLE V.—Series II.

$\theta_1$ .	$\theta_2$ .	$P_1$ in cm. water at 0° C.	$P_2$ in cm. water at 0° C.	Kick of galvanometer.	$\frac{\gamma-1}{\gamma}$ uncorrected for kick of galv.	$\frac{\gamma-1}{\gamma}$ corrected.
383-10	378-49	1084-9	1029-0	6	.2290	.2386
383-20	378-49	1084-2	1029-0	no kick	.2372	—
383-20	378-72	1082-5	1029-0	no kick	.2320	—
383-00	378-48	1091-0	1035-0	4	.2255	.2319
383-00	378-34	1091-6	1035-0	4	.2302	.2366
383-10	378-51	1089-5	1035-0	1	.2349	.2365
383-90	379-47	1098-2	1043-0	1	.2248	.2364
383-90	379-08	1100-4	1043-0	no kick	.2355	—
383-90	379-35	1098-7	1043-0	no kick	.2308	—
383-90	379-50	1099-1	1043-0	3	.2200	.2248
383-90	379-44	1098-9	1043-0	4	.2243	.2307
383-90	379-32	1098-8	1043-0	no kick	.2302	—
383-90	379-22	1099-7	1043-0	1	.2320	.2336
383-90	379-10	1100-6	1043-0	no kick	.2343	—
383-90	379-42	1100-6	1045-0	1	.2266	.2282
383-90	379-38	1100-5	1045-0	1	.2290	.2306
383-90	379-28	1101-5	1045-0	no kick	.2302	—

For these experiments  $\tau = 0.50$  second.

Mean value of  $\frac{\gamma-1}{\gamma} = .2328$ ,

whence  $\gamma = 1.303$ .

The values of  $\gamma$  obtained in these two series of experiments are given for clearness

	$\tau$ in seconds.	$\gamma$ .
Series I. ....	0.67	1.307
Series II. ....	0.50	1.303

The agreement of these observations was not sufficiently close to necessitate the application of the small correction for radiation applied in the air-experiments (correction (2) above). An attempt was made to apply a correction for the heating up of the steam round the thermometer in the time  $\tau$  (correction (1) above). The discrepancies were, however, found

to be too great to render it possible to plot a curve and extrapolate to the value  $\tau=0$ .

It is worthy of mention that the movement of the galvanometer-needle was more rapid in these experiments than in those with air, indicating a quicker rate of heating up of the thermometer. This indication was further confirmed by a third series of experiments which was taken, for which  $\tau$  was 1.14 seconds; the value of  $\gamma$  obtained in this series was 1.291, showing that the thermometer had heated up considerably after 1.14 seconds.

I desire to express my best thanks to Prof. Callendar for his advice and encouragement throughout the course of the work; also to Prof. Porter I am indebted for many valuable suggestions.

#### DISCUSSION.

Prof. CALLENDAR congratulated the Author upon the good agreement of the results of a difficult experiment. He mentioned the difficulties in overcoming conduction when working with steam at a high temperature, and pointed out that the Author's value for the ratio between the specific heats of steam agreed closely with that which he (Prof. Callendar) had recently deduced from theoretical considerations. An important feature of the present paper was that experiments had been performed in which different periods of time elapsed between the releasing of the pressure and the determination of the final temperature. Referring to the fact that the Author had used a platinum thermometer instead of a bolometer strip, he said that although a bolometer strip was more sensitive than a platinum thermometer, it was more sensitive than necessary in such an experiment. Another point in the experiments was the use of smaller quantities of gas than had hitherto been employed, an advantage of importance when dealing with rare gases. Prof. Callendar then exhibited and described the pressure-gauge referred to by the Author and used in his experiments.

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XXXI. *A Suggested Theory of the Aluminium Anode.* By  
W. W. TAYLOR, M.A., D.Sc., and J. K. H. INGLIS,  
M.A., B.Sc.\*

ALTHOUGH aluminium is one of the metals which decompose water, it is very slowly acted upon by dilute sulphuric acid, even at moderately high temperatures. With dilute hydrochloric acid the action is violent, and it is found that, if a little hydrochloric acid or soluble chloride (*e. g.*, potassium chloride) be added to dilute sulphuric acid, the action is, to all appearance, as violent as with hydrochloric acid of similar concentration.

The primary object of this investigation was to find an explanation of this anomalous behaviour of sulphuric acid, and of the effect produced by the addition of chloride. It has long been known † that, when an aluminium electrode is employed as anode in a solution of a sulphate or of sulphuric acid, there is a very great resistance offered to the current, and that this resistance is due to a film which separates the electrode from the solution. If the aluminium is the cathode, or if other acids are substituted for sulphuric acid, this great resistance does not exist. The film cannot merely act as a dead resistance, for the resistance is different according to the direction of the current. It seems probable, then, that the two phenomena are related, and that the film is also the cause of the slow action of sulphuric acid on aluminium. This paper is an attempt to find an explanation which will satisfactorily account for all these phenomena.

*Historical Summary.*

The behaviour of aluminium as anode in dilute sulphuric acid has been the subject of many investigations, but they have been mainly directed to proving the existence of the abnormalities, and not to finding the cause of them. The earliest measurements appear to have been made by Wheatstone ‡, who tried to ascertain the position of aluminium in

\* Read November 14, 1902.

† Buff, Liebig's *Annalen*, cii. p. 269 (1857).

‡ Phil. Mag. [4] x. p. 143 (1854).

the voltaic series. He found that its position depended on the electrolyte used, and he noticed especially the slight action of nitric acid and of sulphuric acid, and the small current obtained with the latter acid. His experiments were repeated in greater detail by Buff\*, who observed remarkable peculiarities with dilute sulphuric acid as the electrolyte. He found on electrolysis of dilute sulphuric acid with an aluminium anode and an external battery, that the anode became covered with a dark skin which he supposed to be silicon. Tait† investigated the polarization of the aluminium cell, using a variable polarizing battery. If six Grove's cells formed the polarizing battery, the reverse E.M.F. was 5.20 Daniells; in this case the polarizing E.M.F. was 10.44 D. As his measurements were made with a Thomson electrometer, they were independent of resistance.

The dark skin first observed by Buff was the subject of several investigations made by Beetz‡. He at first supposed it to be an aluminium suboxide; but, later, came to the conclusion that it is merely the ordinary oxide or hydroxide. More recently Norden§ showed that the film is the ordinary hydroxide,  $\text{Al}(\text{OH})_3$ . Lawrie|| had previously come to the conclusion, based on experiments upon the effect of amalgamation on the electrochemical behaviour of aluminium, that the peculiarities are due to a layer of oxide or of suboxide.

The subject has also been investigated by several physicists who endeavoured to explain the physical peculiarities. At first the film of oxide was supposed to act as a layer which protected the electrode from the action of the electrolyte; but Oberbeck¶ and Streintz\*\* suggested that the film acts as a non-conductor, and that the electrode, the film, and the electrolyte form a condenser; and a condenser consisting of two aluminium plates with a solution of a sulphate as

\* *Loc. cit.* † *Phil. Mag.* [4] xxxviii. p. 243 (1869).

‡ *Pogg. Annalen*, vol. cxxvii. p. 45; vol. clvi. p. 464; 1877, vol. ii. p. 94.

§ *Zeit. für Elektrochemie*, vi. pp. 159, 188 (1899-1900).

|| *Phil. Mag.* [5] xxii. p. 213 (1886).

¶ *Wied. Ann.* xix. p. 625 (1883).

\*\* *Wied. Ann.* xxxii. p. 116 (1887); xxxiv. p. 751 (1888).

electrolyte has been described by Haagn\*. In all these cases a neutral sulphate or sulphuric acid solution formed the electrolyte, Streintz especially mentioning that in nitric acid the behaviour of aluminium is quite normal. The question became one of practical importance when Pollak† and Grätz‡ independently showed that a cell consisting of one aluminium electrode and one carbon electrode in dilute sulphuric acid could be used to change an alternating current into a direct current, since the phase in which aluminium is the anode is stopped by the cell. Various investigators§ found that currents of 20 volts or even of 100 volts potential can be so transformed. Later researches have not brought to light many new facts, though Wilson|| showed that the transformation is not complete if the period of alternation is less than  $\frac{1}{6}$  second. None of the investigators attempt to explain how this film is produced and maintained. Norden¶, however, gives the following explanation:—When sulphuric acid is electrolysed with an aluminium anode the secondary oxygen produced acts on the anode to form  $\text{Al}(\text{OH})_3$ , which is slowly dissolved by the sulphuric acid or by the aluminium sulphate already in solution, and thus the film is continually renewed on one side and dissolved on the other. If hydrochloric acid be used as electrolyte, the free chlorine acts on the aluminium and forms a soluble salt  $\text{AlCl}_3$ , and not a difficultly soluble oxide.—This explanation is hardly sufficient, for no reasons are given for the formation of secondary oxygen; and, further, aluminium sulphate is a fairly soluble salt. Hence a full explanation is still wanting.

### *Experimental Results.*

Experiments were made, in the first instance, to ascertain in what way the addition of certain salts to the electrolyte affected the aluminium anode. For this purpose the 12 volt storage-battery of the laboratory was used, and in the circuit were a

\* *Zeit. für Elektrochemie*, iii. p. 470 (1896-97).

† *Compt. Rend.* cxxiv. p. 1443 (1897).

‡ *Wied. Ann.* lxii. p. 323 (1897).

§ *Bleiblätter*, xxiii. pp. 108, 502, 564, 650; *Elektrotechn. Zeits.* xxi. p. 913.

|| *Electrical Review*, 1898, p. 371; *Proc. Roy. Soc.* vol. lxiii. p. 329 (1898).

¶ *Loc. cit.*

3 ohm (approximate) resistance, an ammeter which could be read to 0.01 ampere and up to 3.0 amperes, and the electrolytic cell, all in series ; a voltmeter reading to 0.05 volt and up to 15.0 volts was also in parallel circuit with the cell. The cell consisted of a beaker containing a 1/1 molar solution of sulphuric acid and the two electrodes, the one of sheet-aluminium, and the other a spiral of thick platinum wire. The procedure was as follows :—The circuit was closed, with the acid alone as electrolyte, and the readings of the voltmeter and ammeter noted as soon as they became constant. To the acid were added successive small quantities of a solution of the salt under investigation ; and, after closing the circuit, readings were noted every few minutes until they again became constant. It was found necessary to use a fresh piece of aluminium each time, as, through the continued action of the weak current, the film on the anode became so thick and resisting that addition of even large quantities of potassium chloride had no influence on the current, although a small quantity only was required when a fresh surface was taken. It was therefore necessary to have the surface in as uniform a condition as possible in order that the experiments should be comparable, and this was most easily ensured by using a fresh surface each time.

*Effect of Chloride and of Bromide.*—The results are given in the following tables.

TABLE I.

Solution of  $H_2SO_4$  = 1 molar.

„ KCl = 3.9 molar (saturated).

Voltmeter in open circuit.	Electrolyte.	Voltmeter in closed circuit.	Current in Amperes.
11.7 volt.	25 c.c. $H_2SO_4$ .....	11.6	0.01
	„ +0.19 c.c. KCl.	11.6	0.02
	„ +0.25 c.c. KCl.	11.6	0.02
	„ +0.33 c.c. KCl.	11.6	0.03
		falling rapidly to 7.1	rising to 1.50
11.7 volt.	25 c.c. saturated ammonium alum solution.....	11.6	<0.01
	„ „ +0.27 c.c. KCl.	9.4	0.76



In the case of ammonium alum solution (Table I.) the effect of potassium bromide was also determined, and after addition of 0.3 c.c. of a 4 molar KBr solution, the current passed freely, though it did not increase so rapidly as after addition of chloride.

The experiments were then repeated with more dilute solutions of chloride and bromide.

TABLE II.  
Solution of  $H_2SO_4 = 1$  molar.  
,,  $KCl = 0.39$  molar.

Voltmeter in open circuit.	Electrolyte.	Voltmeter in closed circuit.	Current in Amperes.
11.7 volt.	25 c.c. $H_2SO_4$ .....	11.65	<0.01
	„ +0.97 c.c. KCl.	11.65	0.01
	„ +2.0 c.c. KCl...	falling to 7.0	rising to 0.50
	„ „ (fresh surface)...	falling rapidly.	rising to 0.80
11.7 volt.	25 c.c. $H_2SO_4$ .....	11.65	<0.01
	„ +1.0 c.c. KCl...	11.60	0.025 (rising)
	„ +1.2 c.c. KCl...	11.60	0.02 (rising)
	„ +1.4 c.c. KCl...	11.60	0.02 (rising)
	„ +1.6 c.c. KCl...	.....	1.0

In the second of these experiments the currents rose at once to 1.0 ampere after addition of 1.6 c.c. KCl solution, but with smaller concentrations of chloride the current was rather variable, as if the resistance of the film was continually changing. In the case of bromide the current did not increase until 5.0 c.c. of a 0.4 molar KBr solution had been added. It then rose steadily to 0.5 ampere, but the increase was not so rapid as with chloride.

Similar experiments were made with other salts, and the results may be very briefly described.

*Nitrate.*—A 2.6 molar solution of potassium nitrate was used. After addition of 3.0 c.c. of the solution to 25 c.c. of acid, the current at once rose steadily; considerable irregularity was shown after addition of 2.0 c.c. of the nitrate solution.

*Acetate.*—Addition of sodium acetate to sulphuric acid had no effect. In order to attain a considerable concentration of

acations, a saturated solution of sodium sulphate was then used instead of sulphuric acid, but this made no difference.

*Thiocyanate*.—A 2·0 molar solution of potassium thiocyanate was used. Addition of 2·0 to 3·0 c.c. of the solution was found necessary to enable the current to pass readily.

*Chlorate*.—Addition of potassium chlorate was also found to enable the current to pass readily.

As the presence of aluminium salt might, conceivably, influence the results, several of the above experiments were repeated after 1·0 c.c. of 0·5 molar aluminium sulphate solution had been added to the acid, but no differences were found.

These experiments show that the presence of certain ions, even in small concentration, enables a large current to pass through the cell; and it seemed to us probable that the reason is that the film of aluminium hydroxide with which the anode is covered is permeable to certain ions, but impermeable to others\*. If this is so, any anion which can readily pass through the film will enable a current to pass, whilst anions which cannot readily pass through will not enable it to do so. The anomalous behaviour in sulphuric acid would then be due to the impermeability of the film to  $\text{SO}_4^{--}$  ions, and also to  $\text{Al}^{+++}$  ions. This explanation is also in accord with the fact that reversal of the current immediately causes a current to pass through the cell, this being due to the permeability of the film to H ions, for it is difficult to suppose that reversal of the current immediately removes the film and subsequent reversal immediately restores it.

We next made a series of experiments to determine the relative rates of diffusion of these ions through a film of aluminium hydroxide. The method adopted is one devised by Walden† and consists in forming a film of gelatine containing ammonium chromate over one end of a glass tube, exposing it to daylight, and then washing out all soluble substances. The tube is then placed in a solution of aluminium salt, and ammonia solution is put inside the tube. In this way a film of  $\text{Al}(\text{OH})_3$  is formed where the two solutions meet, i.e., in the interior of the gelatine. A solution of the salt under examination is then added to the ammonia solution

\* Cf. Ostwald, *Zeit. f. Phys. Chem.* vi. p. 71 (1890).

† *Zeit. f. Physik Chem.* x. p. 699 (1892).

in the inner tube, and from time to time the outer solution is tested for the salt. From the fact that a film of aluminium hydroxide can be formed in this way, one may conclude that it is impermeable to  $\text{Al}^{+++}$  ions, and to  $\text{OH}'$  ions, as otherwise diffusion would continue until one or other of the salts was completely removed.

Having set up a large number of cells we found that  $\text{KCl}$ ,  $\text{KBr}$ ,  $\text{KNO}_3$ ,  $\text{KClO}_3$ , and  $\text{KCNS}$  all diffuse through rapidly, though not equally so;  $\text{NaC}_2\text{H}_3\text{O}_2$  diffuses slowly, and  $\text{K}_2\text{SO}_4$  only to a very slight extent. To confirm this result, more cells were set up, and mixtures of  $\text{KCl}$  and  $\text{K}_2\text{SO}_4$ ,  $\text{KBr}$  and  $\text{K}_2\text{SO}_4$ , were added to the ammonia solution, so that the rates of diffusion through the same film could be observed. The same results were obtained.

It now seemed very probable that the abnormal behaviour of the aluminium anode in sulphuric acid was due to this impermeability. According to Ditte \*, the surface of aluminium is covered with a thin film of hydroxide which preserves it from the further action of the air. If, therefore, a piece of aluminium be made the anode in dilute sulphuric acid, the  $\text{SO}_4''$  ions are unable to pass from the solution through the film to the anode, and similarly  $\text{Al}^{+++}$  ions are unable to pass from the anode into the solution. Hence there are no ions to carry the electricity through the film, and no current can pass. A very slight current does pass, and this may be due to  $\text{Al}^{+++}$  ions being formed at the anode,  $\text{H}^+$  ions of the water passing at the same time through the film and thus leaving  $\text{OH}'$  ions which form  $\text{Al}(\text{OH})_3$  with the  $\text{Al}^{+++}$  ions just formed. This aluminium hydroxide replaces that which may be removed by solution in the acid, and in this way the continuity of the film is maintained.

If  $\text{Cl}'$ ,  $\text{Br}'$ , or  $\text{NO}_3'$  ions are present, they can migrate through the film, thus carrying electricity to the anode where they unite with  $\text{Al}^{+++}$  and form neutral salts; and this formation of salt behind the film will break it loose, and so enable the current to pass easily. In this way the results obtained admit of an easy and rational explanation.

\* *Compt. Rend.* cxxvii. p. 919 (1898).

If this explanation is correct, it should be possible to reproduce the peculiarities of the aluminium electrode with a platinum electrode and a film of aluminium hydroxide. There are various ways in which this might be done, but for practical reasons the following was adopted. The cell consisted of two large pieces of platinum foil as electrodes, an inner porous cell containing ammonia solution (1 molar) and an outer glass beaker containing aluminium sulphate solution ( $\frac{1}{2}$  molar). In this way a film of aluminium hydroxide was deposited in the wall of the porous cell.

If the aluminium sulphate solution contained the anode, no current should pass, since  $\text{Al}^{+++}$  ions cannot migrate through the film to the cathode, nor  $\text{OH}^-$  ions to the anode. Addition of  $\text{SO}_4^{--}$  ions to the ammonia should have no effect on the current, but addition of  $\text{Cl}^-$  ions should cause a current to pass. Reversal of the poles, also, should cause a current to pass, for  $\text{NH}_4^+$  ions can readily pass through the film. With such a cell, and with the 12-volt storage-battery and the same arrangement of apparatus as already described, the following results were obtained :—

Aluminium sulphate solution contained :	Time from closing circuit (minutes).	Voltmeter.	Ammeter.
Anode.	0 60 1140	11.6 12.0 12.0	0.20 0.07 0.03
Cathode.	immediately. 45	11.2 10.4	0.20 0.41
Anode.	10 180	11.7 11.95	0.10 0.03
Cathode.	1.5	10.8	0.43
Anode. Anode.	6 immediately. 4 20	11.7 (50 volt current used.) " "	0.13 0.22 0.07 0.04
Cathode.	immediately.	(50 volta.)	0.83 (42 ohms in circuit.)

The small current which passes is due to the low con-

ductivity of ammonia solution ; so a similar experiment was made with a solution of sodium carbonate in the porous cell, as sodium hydroxide might act on the film. The only difference found was that the maximum current was much greater.

Aluminium sulphate solution contained :	Time from closing circuit (minutes).	Voltmeter.	Ammeter.
Anode.	0	11.3	0.22
	13	11.8	0.07
	65	11.85	0.04
Cathode.	immediately.	10.3	0.5
	3	9.6	0.8
	4	9.1	1.0
Anode.	9	11.8	0.09
	19	11.9	0.06

In the next experiment also sodium carbonate solution was used, and after the current had fallen to 0.07 ampere, part of the sodium carbonate solution was replaced by a saturated solution of potassium chloride. The current increased steadily, after 60 minutes it was 0.35 ampere. On reversal, the current rose immediately to over 2 amperes.

In a similar experiment, after the current had fallen to 0.08 ampere, half of the sodium carbonate solution was removed, and a saturated solution of potassium sulphate added ; even after 60 minutes there was no change in the current. Ammonia was also used in the inner cell, and half of it replaced by saturated solution of potassium sulphate after the current had decreased to 0.04 ampere. After 60 minutes the current was 0.05 ampere, and after 20 hours it was constant at 0.10 ampere. On reversal it immediately rose to over 2 amperes.

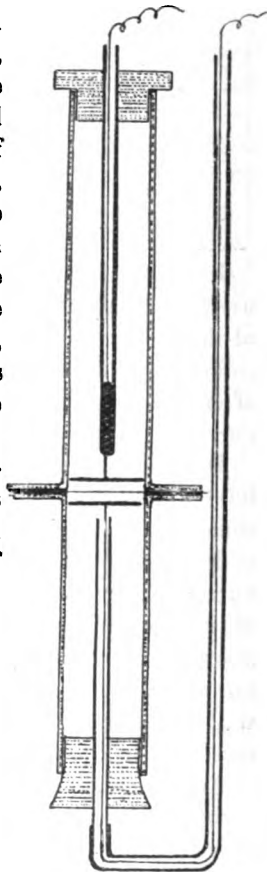
An experiment was also made with solutions of sodium carbonate and aluminium chloride. In this case, after the current had fallen to 0.05 ampere, the poles were reversed and the current increased rapidly (to 0.6 ampere in 1.5 minute) ; but on again reversing, it quickly diminished to its former value.

There is still another way in which the explanation might

be tested—by direct measurement of the resistance which the film offers to the passage of different ions. Suppose that solutions of the four salts  $\text{Al}_2(\text{SO}_4)_3$ ,  $\text{AlCl}_3$ ,  $\text{K}_2\text{SO}_4$ ,  $\text{KCl}$ , be prepared so that they have the same conductivity at say  $25^\circ\text{C}$ ., and that now the two electrodes be separated by a film of  $\text{Al}(\text{OH})_3$ ; then the resistances depend upon the rapidity with which the ions can pass through the film, and the four solutions will, in this case, have different conductivities. The differences should, moreover, be of quite a high order. For in the case of  $\text{Al}_2(\text{SO}_4)_3$ , neither ion would pass through the film, and the resistance measured should be high; in the case of  $\text{AlCl}_3$ , and of  $\text{K}_2\text{SO}_4$ , only one ion could pass through, and the resistances should be of the same order, though much smaller than in the first case. The presence of the film should not make much difference to the resistance of the  $\text{KCl}$  solution, since both ions can pass through; this solution should, therefore, have the smallest resistance.

The apparatus which we used consisted of two glass tubes with flanges ground to fit one another. Between the two tubes was placed a piece of filter-paper which had been soaked in a dilute gelatine solution. The flanges were pressed together while the gelatine was hot, so that a close and water-tight junction was made. Dilute solution of aluminium sulphate was poured into one tube which was closed with a rubber stopper provided with an overflow tube; the apparatus was then reversed and a dilute solution of ammonia was poured into the other tube. In this way a film of  $\text{Al}(\text{OH})_3$  was formed in the gelatinized paper, and after a few hours the whole was carefully washed out with

Fig. 1.



distilled water. One tube was then filled with the solution to be examined, the corresponding electrode adjusted to a definite mark—an overflow tube preventing rupture of the film; the apparatus was then reversed and the other tube filled with the same solution, and the electrode inserted. The whole was placed in a thermostat at 25° C. and measurements of the resistance made. They were as follows :—

$\text{Al}_2(\text{SO}_4)_3$	. . . . .	289 ohms
$\text{AlCl}_3$	. . . . .	259 ohms
$\text{KCl}$	. . . . .	248 ohms

These differences are very small, especially as we found the error of adjustment of the electrodes to be considerable.

It is doubtful if it is practicable to determine these differences with an alternating current. There can be no migration of the ions (with a high frequency and small current), and therefore a very small amount of certain salts in the film is sufficient to enable a current to pass; and will, in fact, largely determine the conductivity. Now the formation of the film by the interaction of the two salts necessarily produces such a salt in the film; and this, no doubt, is very difficult to remove completely by mere washing\*.

We propose therefore to repeat the experiments with a more suitable arrangement of electrodes, and with special preparation of the film. We also hope to make measurements of the resistances using continuous currents.

The explanation of the peculiarities of aluminium when used as an anode in solutions of sulphates, which has thus been suggested, may be applied to the phenomena observed in the reaction between aluminium and dilute acids. But it seemed desirable to determine by experiment whether the presence of those ions which have so marked an influence on the anode has a similar influence on the rate of solution of aluminium in sulphuric acid. Accordingly, the following rough determinations were made of the rate of evolution of

\* With a direct current this salt is removed from the film by the action of the current. This is probably the reason why, in the series of experiments last described, the current *at first* is so long (20 hours) in reaching a minimum, although afterwards it reaches the same minimum in much less time (about the same time that had elapsed between the two previous commutations).

hydrogen from the acid, both alone, and with addition of certain ions.

Preliminary trial showed that at temperatures of  $80^{\circ}\text{C}$ . to  $85^{\circ}\text{C}$ ., and with a 2-molar solution of sulphuric acid, the reaction proceeded at a rate which could be conveniently measured. A thermostat was adjusted to  $85^{\circ}\text{C}$ ., and all the experiments were made at this temperature. Small flasks of about 80 c.c. capacity, and pieces of sheet aluminium of uniform size and weight (25 mm. square, 0.45 gm.) were used. Each flask contained one piece of the metal and 60 c.c. of a 2-molar sulphuric acid solution, and in addition a known quantity of a concentrated solution of the salt under investigation. The gas evolved was collected in a burette. The salts employed were KCl, KBr,  $\text{KNO}_3$ , and KCNS. The results are summarized below.

*Chloride.*—Four experiments were made to determine the effect of chloride, a 3.9 molar solution of potassium chloride being used. The intervals of time required for the evolution of 50 c.c. of hydrogen were

- |                                |  |
|--------------------------------|--|
| (1) 60 c.c. acid.              | 180 minutes, diminishing to 150 minutes. |
| (2) 60 c.c. acid + 1 c.c. KCl. | 70 minutes, diminishing to 50 minutes.   |
| (3) 60 c.c. acid + 2 c.c. KCl. | 2 minutes.                               |
| (4) 60 c.c. acid + 4 c.c. KCl. | 2.5 minutes, diminishing to 1.7 minute.  |

These figures show that chloride has a very decided influence on the velocity of the reaction, but it does not seem to play the part of a simple catalysator. One noticeable feature is that when 2 c.c. of the solution have been added, its maximum effect has been almost reached.

The action may be explained as follows—when a piece of aluminium is put into dilute sulphuric acid, it is covered with a film of hydroxide; this film, being impermeable to  $\text{SO}_4^{2-}$  ions, is impermeable to  $\text{H}^+$  ions also, for the one ion cannot go anywhere without the other. Thus there is no action between the metal and the acid. The aluminium, however, acts slowly on the water in the film, forming hydrogen and aluminium hydroxide, which maintains the continuity of the film. In this way a slow continuous action takes place. If potassium chloride be added to the acid,  $\text{H}^+$  ions can permeate



the membrane, for the  $\text{Cl}'$  ions can go with them, and the metal thus comes in contact with  $\text{H}^+$  ions. This action breaks up the film and so admits the sulphuric acid to the surface of the metal.

If the concentration of  $\text{Cl}'$  ions is too small to cause violent action and so destroy the film, they will still have an accelerating influence, but the maximum effect will not be attained.

*Bromide.*—Addition of bromide appears to have very little influence on the velocity of reaction. Four experiments were made, a 4-molar solution of potassium bromide being used. The times of evolution of 50 c.c. of hydrogen were

(1) 60 c.c. acid	150 minutes.
(2) 60 c.c. acid + 2 c.c. KBr.	160 "
(3) 60 c.c. acid + 4 c.c. KBr.	155 "
(4) 60 c.c. acid (no. 1) + 1 c.c. KBr.	140 "

The fourth experiment was made with the aluminium and acid already used in experiment (1), in order to remove uncertainty as to the uniformity of the surface. Hence the influence of bromide is very slight and the experiments are not sufficient to show whether it accelerates or retards the reaction.

*Nitrate and Thiocyanate.*—These salts were found to have an accelerating effect. With nitrate the reaction was somewhat irregular, and the gas evolved was found to contain nitric oxide. In the case of thiocyanate, hydrogen sulphide was produced in considerable quantity. The results, consequently, are of no value.

Finally, two experiments were made, with acetic acid, and with a mixture of acetic acid and potassium chloride; for according to the theory, presence of chloride should have an accelerating effect. The acetic acid solution was that of maximum conductivity, and the potassium chloride solution was 3.9 molar. The action was very slow and the curves obtained were irregular. In 30 hours 18 c.c. of hydrogen were evolved when acetic acid alone was used, and in the same time 22 c.c. of hydrogen with a mixture of 2 c.c.  $\text{KCl}$  and 60 c.c. of acetic acid.

These experiments must be regarded as rough preliminary observations, and we wish to return to the subject at a later date.

*Summary.*

1. The influence of chloride, bromide, nitrate, acetate, chlorate, and thiocyanate, in varying concentration, on an aluminium anode in sulphuric acid was investigated.
2. A theory to explain the results was brought forward and tested experimentally.
3. The essential peculiarities of an aluminium anode were reproduced by means of a platinum anode and a film of aluminium hydroxide.
4. Some measurements were made to determine the influence of chloride and of bromide, on the reaction between aluminium and sulphuric acid.

Chemical Laboratory,  
University of Edinburgh.  
October 1902.

## DISCUSSION.

Dr. LEHFELDT said that the lines of explanation were probably correct. Referring to the behaviour of an aluminium anode in sulphuric acid, he said that the small amount of conduction might be due to the fact that the film was not quite impermeable.

Prof. S. P. THOMPSON called attention to one of the experiments described in the paper, in which a potential-difference of 50 volts applied to a cell with a membrane of aluminium hydroxide between the electrodes produced a current of 0.07 ampere, and asked what the current would probably have been if the voltage had been reversed.

Mr. CAMPBELL mentioned some experiments which he had seen performed with an aluminium rectifier. He also said that if an alternating E.M.F. of moderate magnitude was applied to the electrodes of a cell consisting of two aluminium plates immersed in strong sulphuric acid, the electrostatic capacity of the cell was large, but if the E.M.F. was increased the capacity fell enormously, and then did not recover on reducing the applied E.M.F. till the cell had been allowed to rest for some considerable time. He asked for an explanation of this phenomenon.

Prof. AYRTON asked the Authors whether the rectifying power of an aluminium anode was a question of resistance or of back E.M.F. He said that if an aluminium anode and a lead cathode were placed in a solution of Rochelle salt and

an E.M.F. applied for about an hour, it was then impossible to send a current through the cell even by increasing the E.M.F. to 120 volts. If such a cell was used as a rectifier, a black deposit was formed on the aluminium plate which remained constant in weight. If a direct current was sent through the cell, a white deposit was formed and the aluminium plate lost in weight. Prof. Ayrton described some experiments which seemed to show that the properties of these cells were connected with changes in the liquids of the cells.

Mr. INGLIS, in reply to Prof. Thompson, said that in the particular experiment referred to a reversal of the E.M.F. would have given a current of about 30 amperes. In the experiment mentioned by Mr. Campbell the explanation might be that when the E.M.F. was large the ions were forced into the interstices of the film and produced an effect corresponding to a diminution of electrostatic capacity. He thought that the power of an aluminium anode as a rectifier was due to increased resistance and not to back E.M.F.

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### XXXII. *A Slide-rule for Powers of Numbers.*

By Prof. JOHN PERRY, F.R.S.\*

[Abstract.]

SOON after Mr. Lanchester showed his Radial Cursor to the Society in 1895 the Author designed this rule and gave it up as inaccurate. It was recalled to his memory by a letter from Brother Bonaventure, of Mount St. Michaels College, Dumfries, who was anxious to have tables of the logarithms of the logarithms of numbers. The Author finds his rule accurate enough for engineering calculations. He replaces the D scale of an ordinary slide-rule by a scale in which the mark  $m$  is placed at a distance representing  $\log \log m$  from the mark 10. The rule exhibited enabled  $m^n$  to be calculated at one operation, where  $m$  is anything from 2 to 1000 and  $n$  is from 0.1 to 10. Again  $m^{\frac{a}{n}}$  or  $m^{\frac{1}{n}}$  or the logarithm of any number to any base or the delogarithization of any number to

\* Read November 28, 1902.

any base can be performed with one setting. When an answer is outside the limits 2 and 1000, two settings are needed. The log. log scale is described by Dr. Roget, Phil. Trans. 1814.

Mr. HARRISON said there could be no doubt that many who had to make calculations would avail themselves of the advantages offered by the addition of the log. log scale to the ordinary slide-rule. He would like to call attention to a further addition by which the general utility of the log. log scale was increased. It was the introduction of a log. ( $-\log$ ) scale which increased the range of the instrument by making it possible to deal with numbers from a small fraction upwards, with the exception of an unavoidable gap near unity. It also made it possible to directly evaluate a quantity like  $a^{-n}$ . In a slide-rule, if the cursor were misplaced by a small amount the consequent error in the reading of the log. scale was, for all positions, the same fraction of the number read. On the other hand, in the log. log scale the proportionate error varied along the scale and was least at the unity end. At the particular place at which the reading is " $e$ " or " $e^{-1}$ " the percentage error agreed with that of the companion log. scale. At any other place where the reading was  $e^n$  the percentage error would be  $n$  times this amount. This proportionate accuracy was exactly that which was justified in dealing with experimental numbers liable to a percentage error. It was always possible to increase the degree of accuracy by splitting the numbers involved into suitable factors. Mr. Harrison also gave some account of the preparation of a ten-inch slide-rule accurate to one part in 300, which he hoped it would be possible to sell for one shilling.

Prof. EVERETT said that the slide-rule exhibited by Prof. Perry would be useful for people constantly engaged in raising numbers to strange indices. For occasional use he thought that a table of logarithms was preferable. He pointed out that a complete history of the slide-rule was given in the introduction to the original edition of Hutton's Tables. There were two distinct methods of using logarithmic scales—one due to Gunter and sensibly the same as that employed in Fuller's spiral rule, and the other that used

in ordinary slide-rules. With his own form of rule, which he found very convenient, it was possible with care to work correctly to one part in four thousand.

Mr. Boys remarked that the slide-rule had occupied his attention for many years. The device employed by the Author for dealing with powers of numbers was perfectly well known, and the log. log scale was usually referred to as the P line. He admitted that the P line was not so much used as it should be, and hoped that the paper would serve a good purpose in drawing attention to it. He thought, however, that in working with gas- and steam-engines Lanchester's rule was eminently suitable for dealing with cases in which numbers must be raised to fractional indices. He agreed with Mr. Harrison's remarks upon the accuracy of the exponential scale, but said that they were apt to create a wrong impression. In dealing with an experimental number subject to error the accuracy obtained by the scale was sufficient, but in raising a true number to a certain power the errors introduced were large. He disagreed with Prof. Perry in his assertion that the ordinary D line was less used than the others.

Prof. GREENHILL thought it would be better to preserve the D line and replace the C line by the log. log scale. He also exhibited the form of Fuller's rule called the R.H.S.

Mr. APPELYARD referred to the advantages of the spiral form of slide-rule, the objections to which are (1) that it is somewhat heavy, and (2) that the cylinders do not always work smoothly, so that there is delay in setting the pointers to the exact position. He suggested that the sliding parts should be arranged on geometric principles, like Lord Kelvin's slides. These principles were applicable both to cylindrical and to straight slide-rules. For the design of cables, the straight slide-rule has especially the merit of enabling  $\log \frac{D}{d}$  to be read off at once.

Mr. COOPER supported Mr. Boys and Prof. Greenhill with reference to the D line, and said he thought it ought not to be abolished.

Prof. S. P. THOMPSON said an exponential rule was a very useful thing in dealing with some of the calculations

connected with alternating currents, more particularly those relating to hysteresis losses. A simple method for carrying out a lot of operations for which the slide-rule is often used, would be to commit to memory the multiplication table up to thirty-three times thirty-three.

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XXXIII. *Photographs of Cross-Sections of Hollow Pencils formed by Oblique Transmission through an Annulus of a Lens.* By Miss ALICE EVERETT.\*

THESE attempts were prompted by reading an interesting paper by Prof. Silvanus Thompson on "Zonal Aberration of Lenses."

The direct rays of an arc light were allowed to pass through an annulus of a simple convex lens tilted to an angle of  $45^\circ$  with their direction, and placed at a distance of about twice its focal length from the arc. The remainder of the lens surface was blocked out by paper gummed on to the glass. The photographic plate was placed at right angles to the course of the beam, and a series of exposures were made at gradually increasing distances from the lens. The room was darkened, the lamp being enclosed in a box with an opening at one end.

The lens used in the first series was a plano-convex of 3'' aperture, and 16'' focus, the plane side being next the light. The free annulus was  $\frac{1}{10}$  of an inch broad, and 1.1 inch mean radius.

In the second series two concentric annuli were employed simultaneously, one near the margin, the other near the centre. The lens in this case was a double convex of  $4\frac{1}{2}$ '' aperture, and about 1 ft. focus.

I have to thank the Authorities of the Davy-Faraday Laboratory for the facilities for making the experiments.

\* Communicated by Prof. Everett, F.R.S.



Fig. 2.

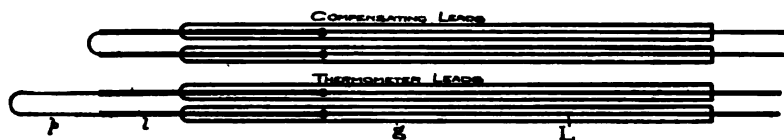


Fig. 3.

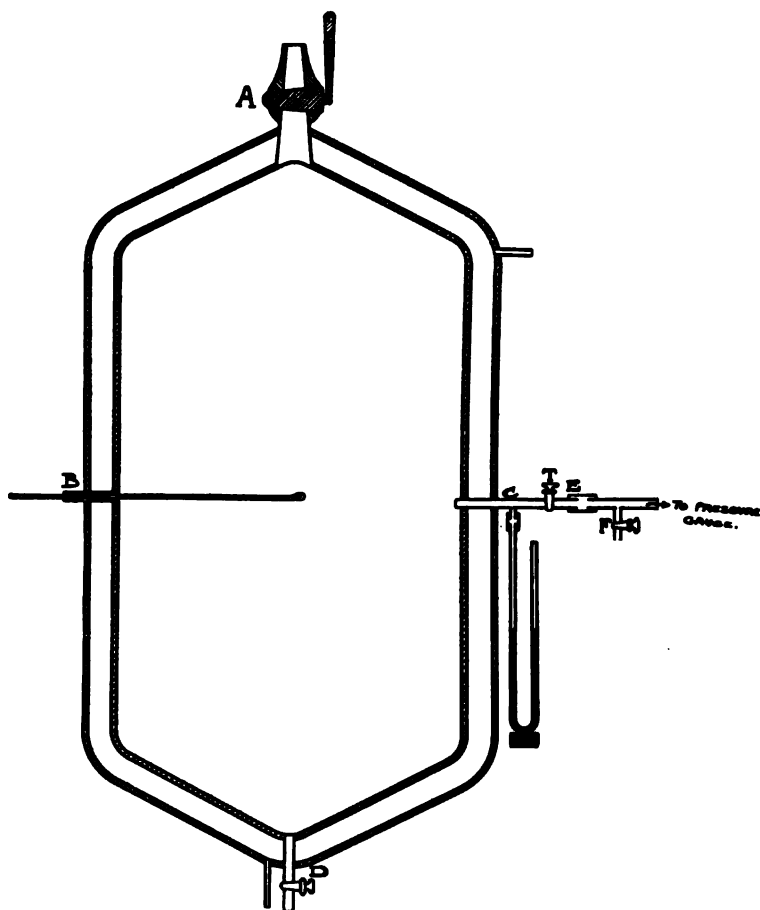
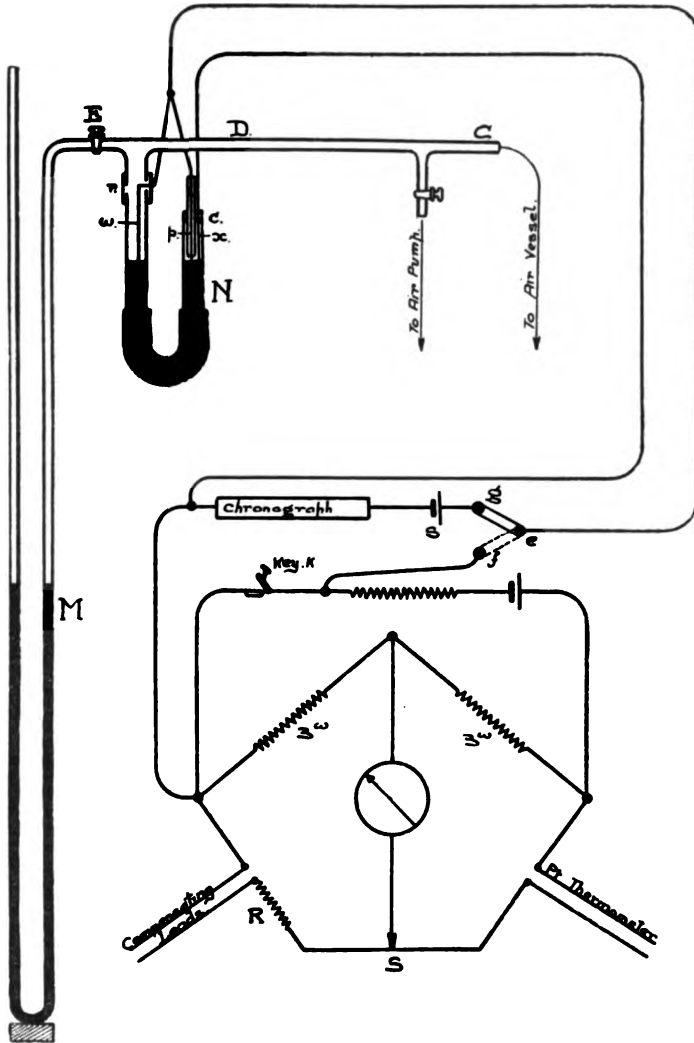




Fig. 1.





XXXIV. *A Portable Capillary Electrometer.* By S. W. J. SMITH, M.A., *Demonstrator in Physics, Royal College of Science, London.\**

[Plate V.]

THIS instrument is a modification of the form of capillary electrometer represented in the first figure, and consisting of two wide tubes joined across by a capillary tube which is cylindrical, and may be horizontal or may slope upwards

Fig. 1.

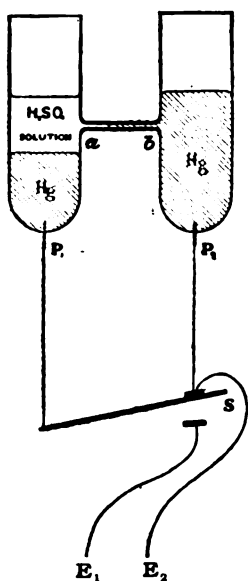
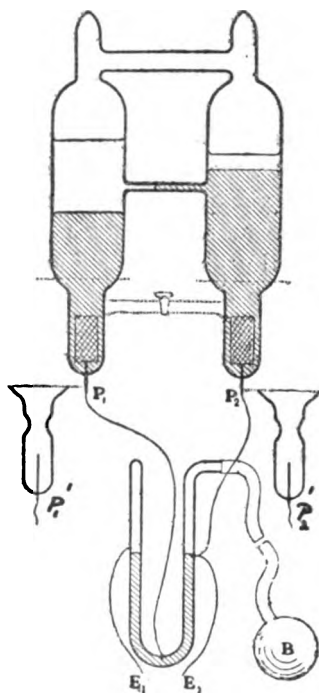


Fig. 2.



at any angle from  $b$  towards  $a$ . The apparatus contains mercury and sulphuric acid of about maximum conductivity distributed roughly as shown. A spring-key, like that represented in the figure, is commonly used with the instrument, and keeps the platinum terminals  $P_1$  and  $P_2$  at the same potential unless the lever  $S$  is depressed. When the lever is depressed the potentials of the terminals become  $E_1$  and

\* Read December 12, 1902.

$E_2$ , which may, for example, be the potentials of two points in a potentiometer circuit. It is the function of the instrument to determine whether these potentials are the same or different.

The nature of the modifications made in the present electrometer is shown in the second figure.

To prevent evaporation of the sulphuric acid solution, without preventing free motion of the liquids within the apparatus, the wide tubes are closed at the top; but are joined across by another tube opening into them as shown. With this arrangement the apparatus is made air-tight, and can, if desired, be made air-free by exhaustion of the apparatus before sealing. It is obvious also that the apparatus can be upset without spilling of the liquid. The two limbs are of equal size, and the capillary passes from the middle of one to the middle of the other. The apparatus contains approximately enough mercury to completely fill one limb, and about half as much sulphuric acid solution. By suitably adjusting the distribution of the mercury and the solution in the two limbs, the apparatus can be arranged for use with the capillary tube either horizontal or tilted upwards at a considerable angle. The maximum angle of tilt available is increased by increasing the lengths of the limbs in comparison with the length of the capillary. It is easy to construct an electrometer which can be used with the capillary at almost any inclination between horizontal and vertical.

The distribution of the mercury can be altered most easily by means of a cross-piece provided with a tap, as represented in the figure by dotted lines. When the tap is open there is free communication between the mercury in the two limbs, and the relative amount in each can be altered by tilting the apparatus. When the tap is closed the two quantities of mercury are insulated from each other. The addition of this arrangement tends to complicate the construction of the instrument, and, although it is very convenient in practice, it is not indispensable. Any desired changes in the distribution of the mercury and the solution can usually be effected without much trouble, by means of the capillary and the upper cross-tube.

To prevent the platinum wires forming the electrodes being wetted by the acid solution, if the apparatus should acci-

dentially, or during transit, be laid on its side or turned upside down, the lower ends of the tubes may be drawn out, as shown at  $P_1'$  and  $P_2'$  in the second figure, and slightly constricted above the ends of the platinum terminals. This precaution may be dispensed with if the electrodes are formed by welding pieces of platinum foil, which are afterwards amalgamated, on to the ends of the wires  $P_1$  and  $P_2$ . The apparatus can then be turned upside down and shaken, so that the amalgamated foil becomes wetted by the acid, without any further ill-effect being produced than an occasional slight wandering of the zero of the instrument for a short time after it is righted again.

The usual spring-key has several disadvantages. Thus, if it is made of brass, the contacts frequently become unsatisfactory through surface tarnishing, and if, to avoid this, the bearing surfaces are made of platinum the key sometimes shows pronounced thermoelectric effects. Further—and this is a point of some importance in a portable instrument—the key cannot conveniently be fastened on to the same stand as the rest of the instrument, for, unless the stand and the support on which it rests are very rigid, the pressure necessary to depress the spring produces sufficient movement of the meniscus, by change in the inclination of the capillary tube during the act of depression, to render the detection of minute changes of surface-tension impossible.

The mercury-key, represented in the second figure, is free from these disadvantages. It consists, as shown, of a U-tube closed at one end and communicating at the other with a pneumatic-pressure ball and containing mercury in the bend. Three platinum wires are fused into the tube and connected as shown. It is obvious that the same change of contacts is produced by squeezing the ball B, as by depressing the lever S in the spring-key. The mercury in this key takes the place of the lever in the spring-key, and the two different contacts between it and  $E_1$  and  $E_2$  respectively are here quite definite and practically independent of the amount of pressure exerted upon the ball B. Further, the contacts are not exposed directly to the laboratory atmosphere. The thermoelectric effects are very small since the changing contacts take place between platinum and mercury which are almost identical thermoelectrically. The warmth com-

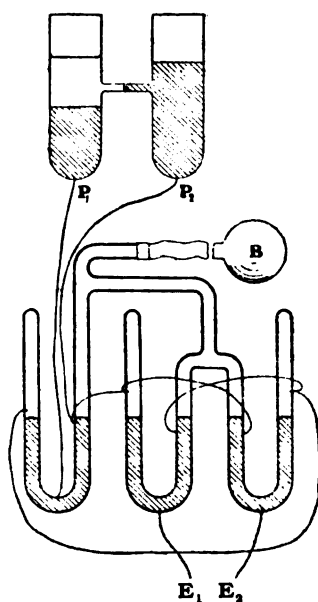
municated to the key from the hand of the operator can be neglected, and the heat produced by the compression of the air in the key need only be very small. The key can be fixed to the same stand as the rest of the apparatus, for even if the pressure which changes the contacts is applied as suddenly as possible the maximum vertical pressure upon the stand is only a few grams, whereas in the case of the ordinary spring-key it may be 500 grams or more.

By adjusting the length of the mercury column in the key so that it is only slightly less than the length of the U-tube between the two extreme platinum wires, the change of potential at  $P_1$  from  $E_2$  to  $E_1$ , and conversely, can be made almost instantaneously. Hence measurements can be made with the instrument even if the zero is altering fairly rapidly. With a key of this kind it is also obvious that the observation of the meniscus through the microscope can receive a very near approach to undivided attention.

Commutators and keys which make a set of connexions in a prescribed order can be constructed on the same principle as the pneumatic key above described. The third figure represents a combined commutator and electrometer key.

The U-tube to the left is the key already described, and the double U-tube to the right is the commutator. The positions of the different wires are so arranged with respect to the levels of the mercury, that it requires greater pressure to change the contacts in the double U-tube, than in the tube to the left. The first effect of pressure is to throw the electrometer into the potentiometer or other circuit, connecting  $P_1$  with  $E_1$  and  $P_2$  with  $E_2$ . On increasing the pressure, the connexions in the double U-tube are reversed and  $P_1$  is con-

Fig. 3.



nected with  $E_2$  and  $P_2$  with  $E_1$ . Hence, when the contacts change in the commutator, we get a motion of the electrometer meniscus corresponding to approximately twice the difference of potential between  $E_1$  and  $E_2$ , and so, in this way, the sensitiveness of the instrument is doubled.

While it is clear that to get the minimum thermoelectric effect in mercury-platinum keys, it would be necessary to use a method of changing the contacts in which compression of air in the key does not take place, yet the thermoelectric electromotive forces which occur in the pneumatic keys described are much too small to produce an observable effect upon the readings of the most sensitive capillary electrometer\*.

The sensitiveness of the electrometer, using the simple key first described, is such that when the diameter of the wide tubes is about 1 cm. and the diameter of the capillary is about 1 mm., a movement of the meniscus perceptible with certainty in a microscope magnifying 100 times is produced by a potential-difference equal to .0001 volt. The actual extent of the movement is somewhat variable, and amounts usually to about .01 mm. The following numbers, obtained with apparatus previously described (Phil. Trans. A. 1899, vol. cxiii. p. 63), show the effect of comparatively large polarizing electromotive forces upon the surface-tension between mercury and sulphuric acid solution of density 1.17 :—

E.M.F. Volts.	Surface-Tension.
0	$\gamma$
0.0202	1.021 $\gamma$
0.0404	1.040 $\gamma$
0.0605	1.059 $\gamma$
0.0807	1.080 $\gamma$
0.1009	1.097 $\gamma$

$\gamma$  is the "natural" surface-tension between the mercury and the solution. Its approximate value is 300 ergs per sq. cm. Judging from these numbers, it would seem that the surface-tension is altered by about one part in 10,000 by a polarizing

\* Since this paper was read I have found that mercury keys (similar in principle to those referred to above) in which the thermoelectric effects are reduced to a minimum are described by Kamerlingh Onnes, *Leyden Communications*, No. 27, p. 31, 1896.

E.M.F. of .0001 volt. In the case in which the capillary-tube is horizontal and the wide tubes are vertical, the relation between the motion of the meniscus  $\delta x$  and the corresponding change in surface-tension  $\delta \gamma$  is expressed approximately by

$$a^2 \rho g \delta x = A c \delta \gamma$$

if we assume that the capillary and wide tubes are of uniform cross-section— $a$  being the area of cross-section of the capillary,  $c$  its circumference,  $A$  the area of cross-section of the wide tubes, and  $\rho$  the sum of the densities of the mercury and the solution. From this formula it would appear possible to produce a much larger movement of the meniscus than .01 mm. by means of a potential-difference of .0001 volt by using a very narrow capillary, especially if the cross-section of the capillary were elliptical instead of circular. It is found in practice, however, that the motion of the meniscus under minute polarizing forces is controlled very largely by stickiness and accompanying changes in the angle of contact between the liquids and the glass, and by variation in the cross-section of the tube at the place where the meniscus rests. The sensitiveness of the instrument to small electromotive forces is practically as great when the diameter of the capillary is 1 mm. as when it is very much less. A very narrow capillary is less easy to manipulate than a comparatively wide one (about 1 mm. in diameter) and is only advantageous when it is desirable that the capacity of the instrument should be as small as possible, or that its action should be as rapid as possible. In the latter case the length of the capillary should also be small.

If the capillary-tube, instead of being horizontal, is inclined at an angle  $\theta$  to the horizontal, the equation given above becomes

$$a g \{ (\rho_1 + \rho_2) a / A \cdot \cos \theta + (\rho_1 - \rho_2) \sin \theta \} \delta x = c \delta \gamma,$$

in which  $\rho_1$  is the density of the mercury, and  $\rho_2$  that of the solution. From this equation it follows: (1) that if  $\theta$  is positive (mercury thread sloping upwards towards the meniscus) the sensitiveness is not increased appreciably by making  $A$  very large in comparison with  $a$ , unless  $\theta$  is very small; and (2) that if  $\theta$  is negative (meniscus at lowest part of thread) the mercury becomes unstable when  $\theta$  is numerically greater than  $\tan^{-1} (\rho_1 + \rho_2) a / (\rho_1 - \rho_2) A$ , *i. e.* when  $\theta$  is numerically



greater than  $a/A$  approximately, since in order that the polarization may be practically confined to the capillary electrode, the ratio  $a/A$  must be small. It also follows that if it were proposed to design an instrument which should have the utmost sensitiveness possible, attention would have to be paid to the straightness of the capillary as well as to the uniformity of its cross-section. It is not necessary, however, to take the precautions here indicated in order to obtain the sensitiveness already quoted; it may be obtained with almost any capillary-tube chosen at random, and with  $\theta$  having such a positive value that the restoring force for a small displacement is considerable enough to render the instrument easy to work with.

The sensitiveness of  $\cdot 0001$  volt, which is obtainable without any difficulty if the mercury is clean, is sufficient for a great many measurements in which the electrometer can be employed, and for these the electrometer (which for the purpose in question is really a surface-tension galvanometer) is more convenient than an ordinary galvanometer with a suspended magnetic system. The electrometer is much more easily set up than an ordinary galvanometer. There is no suspension, no lamp and scale, and, practically, no levelling; but it is advisable when working with the instrument that the potential of  $E_1$  should never be more than a few tenths of a volt less, or more than about a volt greater, than the potential of  $E_2$ . These conditions of working are, in general, not difficult to satisfy. If the potential-differences applied exceed either of the limits above mentioned, it is sometimes necessary to run some of the mercury through the capillary tube in order to get the instrument again into its best working order. The capillary electrometer is already used almost universally in physico-chemical laboratories, and the modifications herein suggested may, perhaps, have the effect of slightly extending the sphere of its usefulness. The accompanying Plate V., taken from a photograph, represents one form of the instrument described. Its size is about two-fifths of that of the actual instrument. The arrangement of the different parts will be obvious from the description already given. The illumination of the end of the mercury-thread is effected by means of a concave mirror attached to the base of the instrument.

## DISCUSSION.

Dr. R. T. GLAZEBROOK congratulated the author, and said that workers with the capillary electrometer would appreciate the improvements introduced. He said that the author had given the minimum E.M.F. which the instrument could detect, and asked what was the maximum E.M.F. which could be safely applied. He referred to the advantages of the mercury keys exhibited, and remarked that, by their use, many difficulties were obviated.

Dr. LEHFELDT said the mercury keys were improvements on those used by Prof. Onnes. In these keys the contacts were changed by the motion of mercury brought about by tilting. The tubes containing the mercury were exhausted to prevent oxidation.

Mr. SMITH, in reply to Dr. Glazebrook, said that, roughly, the maximum E.M.F. should not exceed half a volt.

*XXXV. Note on an Elementary Treatment of Conducting Networks. By L. R. WILBERFORCE, M.A., Professor of Physics at University College, Liverpool\*.*

It may be worth while to point out that the well-known reciprocal relations between the parts of a conducting network can be readily established without an appeal to the properties of determinants.

Let A, B, C, D, ..., be a number of points connected by conductors AB, AC, AD, ..., BC, BD, ..., CD, ..., of resistances  $R_{AB}$ , ..., and suppose that currents  $Q_A$ , ..., are led into the network at the points A, ..., from without, subject to the condition  $Q_A + Q_B + \dots = 0$ , and that internal electromotive forces,  $E_{AB}$ , ..., act in the conductors in the directions AB, .... Let the currents in the conductors be  $C_{AB}$ , ..., and let the potentials at A, ..., be  $V_A$ , .... The fact that there is no continuous accumulation of electricity at any point gives us a series of equations whose type is:—

$$Q_A = C_{AB} + C_{AC} + \dots \quad (1)$$

and the application of Ohm's law gives us a series whose type is

$$R_{AB} C_{AB} = V_A - V_B + E_{AB} \quad (2)$$

\* Read January 23, 1903.

Suppose now that a different system of external currents,  $Q'_A, \dots$ , and internal electromotive forces,  $E'_{AB}, \dots$ , are applied to the same network, and let the consequent currents and potentials be denoted by accented letters. Equations similar to (1) and (2) will, of course, hold for these quantities.

Multiplying each equation of series (2) by the corresponding current in the second system and adding, we obtain :—

$$\Sigma R_{AB} C_{AB} C'_{AB} = \Sigma C'_{AB} (V_A - V_B) + \Sigma E_{AB} C'_{AB}.$$

Now, remembering that  $C'_{NM} = -C'_{MN}$ , the coefficient of any potential  $V_M$  on the right-hand side of this equation is easily seen to be  $C'_{MA} + C'_{MB} + \dots$ , and thus is  $Q'_M$ . The equation thus becomes :—

$$\Sigma R_{AB} C_{AB} C'_{AB} = \Sigma V_A Q'_A + \Sigma E_{AB} C'_{AB}.$$

By a similar process we obtain

$$\Sigma R_{AB} C_{AB} C'_{AB} = \Sigma V'_A Q_A + \Sigma E'_{AB} C_{AB}.$$

[If the accented system is made to coincide with the unaccented system, we obtain  $\Sigma R_{AB} C^2_{AB} = \Sigma V_A Q_A + \Sigma E_{AB} C_{AB}$ , the equation of activity.]

From the general equation :

$$\Sigma V_A Q'_A + \Sigma E_{AB} C'_{AB} = \Sigma V'_A Q_A + \Sigma E'_{AB} C_{AB}$$

the required reciprocal relations follow at once.

(i.) Let every  $Q$  and  $Q'$  be zero, and every  $E$  except  $E_{AB}$ , and every  $E'$  except  $E'_{CD}$ .

Then :  $E_{AB} C'_{AB} = E'_{CD} C_{CD}$ , and if  $E_{AB} = \pm E'_{CD}$  then  $C_{CD} = \pm C'_{AB}$ , or, in words, if an E.M.F. in one branch produces a certain current in a second branch, then an equal E.M.F. in the second branch will produce an equal current in the first ; and, according as the direction of the latter E.M.F. is the same as or opposite to that of the former current, the direction of the latter current will be the same as or opposite to that of the former E.M.F. Again, if  $C_{CD}$  is zero,  $C'_{AB}$  will be zero, which leads to the definition of conjugate conductors.

(ii.) Let every  $E$  and  $E'$  be zero, and every  $Q$  except  $Q_A$  and  $Q_B$  (which will be  $-Q_A$ ), and every  $Q'$  except  $Q'_C$  and  $Q'_D$  (which will be  $-Q'_C$ ).

Then :  $(V_C - V_D) Q'_C = (V'_A - V'_B) Q_A$ , and if  $Q_A = Q'_C$ ,  $V_C - V_D = V'_A - V'_B$ ; that is, if a certain current led in at  $A$  and out at  $B$  produces a certain excess of potential of  $C$  over  $D$ , an equal current led in at  $C$  and out at  $D$  will produce an equal excess of potential of  $A$  over  $B$ .

## DISCUSSION.

Mr. T. H. BLAKESLEY said that Prof. Wilberforce's results might be arrived at by the generalization (which Mr. Blakesley had arrived at) that if any two conductors in a network are considered, one as possessing the seat of an E.M.F. and the other as deriving a current on that account, the remainder of the network might be replaced by four conductors joining the ends of the two conductors under consideration, and so constituting a six-conductor arrangement as in a Wheatstone's bridge. Maxwell was aware of the results, though he arrived at them by a line of thought different from that employed by Prof. Wilberforce.

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XXXVI. *On the Measurement of Small Capacities and Inductances.* By J. A. FLEMING, D.Sc., F.R.S., Professor of Electrical Engineering in University College, London, and W. C. CLINTON, B.Sc., Demonstrator in the Pender Electrical Laboratory, University College, London\*.

[Plate VI.]

THE measurement of small capacities and inductances has become important in connexion with Hertzian Wave Wireless Telegraphy. The experimental determination of the electrical capacity of telegraph wires and of the overhead wires used for the conveyance of high tension alternating currents, is also called for in connexion with the calculation of sending speeds and of voltage drop in a power line. The advantage of possessing an appliance which will conduct this work quickly and well has led us to design the instrument which is here described.

It is generally admitted that for the measurement of small capacities, when the dielectric is air or some other substance not possessing the quality commonly called absorption, no method is so easy to apply as that depending upon the rapid charge and discharge of a condenser through a galvanometer.

\* Read February 27, 1903.

This method is almost the only one applicable to the measurement of the small electrical capacities of wires insulated in the air, such as the aerial wires employed in Hertzian Wave Telegraphy, or ordinary telegraph-wires, or small air-condensers, or in fact any form of condenser in which the capacity is independent of the time of charging. This method has been extensively employed, the only difference being in the nature of the commutator for charging and discharging the condenser. Maxwell suggested the use of a tuning-fork as a switch, the vibrating prongs being furnished with a stylus which made and broke contact with a mercury cup, or vibrated to and fro between two fixed contacts. The great objection to this arrangement is the uncertain duration of the contact. Hence other experimentalists have employed an electrically maintained tuning-fork with a vibrating contact used as a means of driving synchronously an electromagnetic contact-breaker, which in turn makes a better and longer contact between two stops alternately. A device of this latter kind was successfully employed by Professor J. J. Thomson \*, Dr. Glazebrook †, and Professors Fleming and Dewar ‡ in various experiments connected with the measurement of specific inductive capacity at low temperatures.

We have had considerable experience with all these tuning-fork devices, but we have found them troublesome in practice, especially when a large number of measurements have to be made. In addition there is always an uncertainty as to the actual duration of the contact, which makes it impossible to determine by calculation whether the condenser is being fully discharged at each vibration. After a great many preliminary experiments, we finally devised the following

\* See J. J. Thomson, *Phil. Trans. Roy. Soc.* 1883, p. 718, "On the number of Electrostatic Units in the Electromagnetic Unity of Electricity."

† Also R. T. Glazebrook, *Phil. Mag.* Aug. 1884, vol. xviii. p. 98, "On a Method of measuring the Capacity of a Condenser"; or *Proc. Brit. Assoc.* Leeds, 1890.

‡ J. A. Fleming and J. Dewar, *Proc. Roy. Soc. London*, 1896, vol. lx. p. 368, "On the Dielectric Constant of Liquid Oxygen and Liquid Air."

appliance, which when properly made never fails to give satisfaction and renders the measurement of small capacities, even as small as one ten-thousandth of a microfarad, a matter as easy as the measurement of resistance on a Wheatstone bridge.

The instrument as constructed consists of a continuous current electric motor of  $\frac{1}{4}$  HP., but for certain purposes, and where very small capacities have to be measured, it is preferable to employ a motor of  $\frac{1}{2}$  HP. This motor is bolted down upon a baseboard and has connected with it a starting and regulating resistance. The motor is preferably 100 or 200 volt shunt wound motor. To the shaft of this motor is connected by a flexible coupling the commutating arrangement, the function of which is to charge the capacity or condenser to a given voltage and then discharge it through a galvanometer, repeating this process four times in each revolution of the motor. This commutator is fixed on a shaft carried in well lubricated bearings supported on two small A frames (Pl. VI. fig. 1). On this shaft are held, by means of ebonite bushes and washers, three gunmetal disks or wheels, of which the centre one is in shape like an eight-rayed star, whilst the two outer ones are like crown wheels, each having four teeth. The three wheels are so set on the shaft that the teeth or projections of each of the two outer wheels interlock or fall in the space between the teeth of the other, whilst the radial teeth of the intermediate wheel occupy the intervals between the teeth of the two outer wheels. The developed surface of this triple wheel is shown in fig. 2. The whole outer surface is turned true and forms a barrel about four inches in diameter, and two and a half inches wide. On this barrel rest three brass gauze brushes which are carried in well insulated brush holders, and by means of three springs and levers the brushes are firmly pressed against the barrel, the two outer brushes resting on the continuous portions or flanges of the two outer wheels A and B, and the middle brush occupying the centre line and making contact either with the wheel A or wheel B, or with the intermediate wheel I according to their position. It will be seen then that as the commutator runs round, the middle brush is alternately brought into metallic connexion with first one and

then the other of the two brushes on either side. The function of the middle wheel (I) is to afford a stepping piece and prevent any shock or jar as the middle brush passes over from one connexion to the other. It also prevents the middle brush from short-circuiting the two outer brushes at any time. If then one terminal of the galvanometer is connected to the brush pressing against the wheel A, and one terminal of a battery is connected to the brush pressing against wheel B, and one terminal of a condenser is connected to the middle brush, the other terminals of the battery, galvanometer, and condenser being connected together, it will easily be seen that as the commutator runs round, the condenser is first charged at the battery, and then discharged through the galvanometer. In the following experiments, speeds of 1200 to 1700 revolutions per minute were used. To count the rotations of the commutator a worm on the shaft drives a wheel of such gear that the latter makes one revolution for every hundred revolutions of the commutator. This wheel carries a pin which at each revolution causes a hammer to strike a gong. Every hundred revolutions, therefore, of the motor or commutator, the gong gives one stroke, and by means of a stop-watch it is easy to take the time of ten strokes of the gong ; in other words, to ascertain the time in seconds of a thousand revolutions of the motor, and therefore of the number of commutations per second. In the case of the motor we have employed, 1000 revolutions take place generally in 40 seconds, which is at the rate of 1500 per minute, and therefore corresponds with 100 commutations of the condenser per second.

We have tried various methods of making the rubbing contacts and found nothing better than brass gauze brushes. Carbon brushes were tried at one time and found to be unsuccessful. It is essential that the commutator surface should be kept bright and clean, and the brass gauze brushes do this themselves when adjusted to the right pressure.

Associated with this commutator we have employed a galvanometer of the movable coil type, either one made by Crompton, or in some cases one made by Pitkin. By the aid of this instrument, given a source of constant voltage by which the motor can be driven steadily, such as a secondary

battery, the measurement of small capacities becomes an exceedingly easy matter.

There is, of course, no novelty in the mere use of a rotating commutator for the determination of capacities by the above method. It was employed many years ago by Dr. R. T. Glazebrook for this purpose. See 'The Electrician,' vol. xxv. p. 616, 1890, on "The Air Condensers of the British Association." One of us (Dr. Fleming) had, however, employed the device several years previously for the same purpose. Our only claim to novelty in this matter is that of having worked out a thoroughly satisfactory form of rotating commutator, which is designed more from the point of view of an engineer than an electrical instrument maker.

In the case of the measurement of capacity of insulated wires or aërials, the aerial is connected to the middle brush, one terminal of the galvanometer and battery respectively are connected to the two remaining brushes, and the other terminals of the galvanometer and battery are connected to the earth (see fig. 3). Under these circumstances, when the commutator is in rotation, the galvanometer gives a perfectly steady deflexion due to the passage through it of 100 discharges per second from the condenser. In order to determine the numerical value of the capacity, we have therefore to evaluate the deflexion of the galvanometer and to determine the ampere value of a steady current which will make the same deflexion. This can be accomplished by putting the galvanometer in series with a variable resistance, and placing the two as a shunt on a known small resistance in series with another variable resistance, and then placing on the terminals of this circuit a cell of known electromotive force.

In the case of most movable coil galvanometers, the scale deflexions are by no means proportional to the current, and hence when measuring a series of capacities it is desirable afterwards to plot a calibration curve of the galvanometer scale, from which the condenser currents can be read off directly in microamperes. This, however, is always easily accomplished. In addition, we have to measure the potential of the discharging battery. For most practical purposes this can be done by a Weston voltmeter.



Thus let  $V$  represent the voltage of the battery charging the condenser or aerial,  $C$  the capacity of the condenser in microfarads,  $A$  the current in microamperes through the galvanometer,  $n$  the number of charges per second, then

$$A = nCV$$

or  $C = A/nV.$

In order to avoid the necessity for standardizing the galvanometer and measuring the voltage of the charging battery, we have devised a method employing a differential galvanometer which in principle is as follows:—The condenser discharges, as above described, pass through one coil of the differential galvanometer, the other coil being traversed by a current taken from the same battery, and therefore having the same voltage. This second coil is shunted by means of a shunt  $R$  and has in series with it a high resistance  $r$ . If then these resistances are arranged so that the galvanometer shows no deflexion, we have the following equation for the capacity:—

$$\frac{nVC}{10^6} = \frac{V}{r + \frac{GS}{G+S}}$$

$$C = \frac{(G+S)10^6}{nr(G+S) + nGS}$$

This determines the capacity in terms of a conductance and the reciprocal of a time, thus reducing the number of dimensional quantities to be measured to the minimum.

In carrying out this method, it is perfectly impossible to use any ordinary differential galvanometer, because with an electromotive force of 100 volts or more between the coils the resulting unavoidable leakage entirely vitiates the result. We have therefore devised a differential movable coil galvanometer which has been made for us by Messrs. James Pitkin & Co., and is constructed as follows:—

In this galvanometer there are two sets of fixed field-magnets, and also two movable galvanometer-coils completely insulated from one another, but attached to the same stem, which also carries the mirror. Very fine spiral flexible wires convey the currents into and out of each coil. In order to

make the galvanometer differential and therefore show no deflexion when the same current is passed in opposite directions through the coils, it is necessary to be able to adjust exactly the field-strength in the air-gap of the fixed magnets. This we accomplish by means of two curved pieces of soft iron P, which are moved by screws to or from the field-magnets N, S (Pl. VI. fig. 4) so as to shunt more or less of the lines of flux passing between the pole-pieces of the magnet. In this manner we find we can construct a movable coil differential galvanometer which shows no deflexion when the same or equal currents are passed in opposite directions through the two coils, yet each coil is perfectly insulated from the other.

Employing such a differential movable coil galvanometer in connexion with a commutator, we get rid of all necessity for measuring any voltage or electromotive force, and reduce the measurement of capacity simply to a determination of the speed of the commutator (which can be taken with great accuracy by means of a stop-watch) and the known value of the shunt and series resistances in connexion with one coil of the galvanometer. Moreover, we can always tell from the speed of the commutator exactly the time during which the condenser is in connexion with the galvanometer, and hence whether the time of contact is, as it should be, large compared with the time-constant of the discharge circuit.

We have employed one or other of these methods in making a number of measurements of the capacity of aerial wires, such as are used in connexion with Hertzian Wave Telegraphy, and also in the investigation of the laws governing the capacity of such wires when grouped together in certain ways, and we have employed the arrangements for verifying experimentally, as far as possible, the formulæ that have been given for the capacity of insulated wires in various positions in regard to the earth. Taking first the case of single vertical wires insulated in the air, measurements have been made of the capacity of wires suspended vertically in the open air, and also in the interior of a large Laboratory, the dimensions of which are 18 feet high, 32 feet wide, and 44 feet long.

Some preliminary experiments in the open air showed that the capacity of parallel wires suspended in the air, and

insulated, is by no means equal to the sum of their separate capacities when in free space, even when the wires are not very near together. A series of experiments was therefore carried out in the Pender Laboratory with flat iron strips, to investigate this fact more carefully. Eleven lengths of iron strip one inch wide, the thickness being 0.05 inch, and 15 feet 4 inches long, were suspended vertically from the ceiling of the Laboratory by silk strings passing over porcelain buttons. To keep the strips straight they were fastened to the floor through pieces of ebonite. Connexion was made at the bottom end of each strip by a terminal to a straight bare copper wire connected to the above described commutator, so that the capacity of any one strip or of any number of strips in parallel could be measured. In the first place, the individual capacity of each strip taken alone and isolated, was measured and found to be nearly the same in each case. Hence in the tabulated results, the absolute values of capacity are not given, but the capacity of each of the above strips by itself in the room, and held vertically, is taken as unity. The voltage of the battery employed in charging the strips was about 148 volts, and the number of revolutions of the commutator 1200 per minute, corresponding to a frequency of 80. One terminal of the insulated battery used for charging was connected to the earth, and also one end of the galvanometer. The other ends of the galvanometer and battery were connected to the outside brushes on the commutator, the middle brush being connected to the insulated strip or strips. A series of capacity measurements was made, taking the strips one at a time, two at a time, three at a time, &c., and at various distances apart, viz.: 12, 6, and 3 inches, and also when close together. The results are tabulated in the following table (p. 394).

The last column in the Table gives the figures showing the sum of the individual capacities of the strips, and it will be seen that the total measured capacity of  $n$  strips taken together at a distance  $d$  inches apart is always very much less than the sum of the individual capacities of the  $n$  strips, that is, much less than  $n$  times the capacity of one strip, and the figures show that as the strips are brought nearer together this difference increases. When the strips are about 6 inches

TABLE I.—Measurement of the Capacity of Flat Iron Strips suspended in a large room, taken separately and together, at various distances apart.

Number of strips taken in parallel.	Measured Total Electrical Capacity with distance between strips as below stated.				Sum of the separate individual capacities.
	12-in.	6-in.	3-in.	Close together.	
1 .....	1.00	1.00	1.00	1.00	1.0
2 .....	1.74	1.45	1.34	1.19	2.0
3 .....	2.31	1.80	1.61	1.27	3.0
4 .....	2.79	2.10	1.85	1.44	4.0
5 .....	3.28	2.42	2.03	1.46	5.0
6 .....	3.75	2.70	2.21	1.54	6.0
7 .....	4.18	2.98	2.36	1.59	7.0
8 .....	4.61	3.25	2.52	1.72	8.0
9 .....	5.03	3.51	2.68	1.81	9.0
10 .....	5.46	3.76	2.82	1.96	10.0
11 .....	5.90	4.00	2.97	1.99	11.0

apart, that is to say, separated by a distance equal to about 3 per cent. of their length, the capacity of the strips in parallel is very nearly proportional to the square root of the number of strips; thus, four strips have only twice the capacity of one strip, and nine strips rather more than three times the capacity of one strip. The same fact has been observed by us in the case of the measurements of the capacity of wires suspended in the open air. Taking for convenience as a unit of small capacity the micro-microfarad (M.M.Fd.), i. e., the millionth part of one microfarad, we have made measurements of the capacity of nearly vertical insulated wires suspended in the air, with their lower ends a few feet from the ground, and have obtained the following results. In these measurements the capacity measured was that of the wire or body under investigation, together with that of a connecting wire, and that of the commutator itself. This latter quantity is about 60 micro-microfarads, and that of the commutator and lead used varied from 80 to 300 M.M.Fd., according to the length of lead. This value is subtracted from the observed total value. The capacity of a wire one-tenth of an inch in diameter and 111 feet long, with the bottom end about 5 feet from the ground,

was found to be 205 micro-microfarads. In the next place, 160 wires of the same kind and diameter, but 100 feet long, were arranged in a conical form, so that the common junction of all the wires was about 10 feet from the ground, and the tops of all the wires were distributed around a square of 80 feet side, and at a height of about 112 feet from the ground, the wires being therefore about 2 feet apart at the top, and in nearly close contact at the bottom. Such an arrangement of insulated wires was found to have a capacity of 2685 micro-microfarads; in other words, about thirteen times that of one wire, so that in this case the square-root law also holds very closely. In the same way the capacity of four parallel vertical wires 111 feet long, and one-tenth of an inch in diameter, arranged vertically at the corners of a square of six feet in the side, was measured, and was found to be 583 micro-microfarads; in other words, about two and a half times the capacity of one single wire of the same kind in the same position. Similar measurements have shown that 25 wires 200 feet long, arranged with their bottom ends close together, and about ten feet above the ground, and their top ends about two feet apart, had a capacity not greater than five times that of one single wire of the same kind in the same position. Hence it is clear that in bunching together or placing in contiguity a number of vertical wires in the air so as to form a radiator for use in Hertzian Wave Wireless Telegraphy, account must be taken of this fact, and the assumption must not be made that the capacity of  $n$  parallel wires placed vertically in the air and insulated, even approaches a value equal to the sum of their individual capacities, unless the distance between the wires is a large percentage of their length.

This effect was further examined in another series of experiments made in the Laboratory. Two of the above-mentioned iron strips, suspended and insulated as before, were placed at different distances apart, and their united capacity measured and compared with the mean value of their separate capacities. Taking this mean value of the capacity of a single strip as unity throughout, the results are as follows :—

TABLE II.

Horizontal distance between strips in inches. Strips 174 inches long.	Horizontal distance between strips as a percentage of their length.	Capacity of the two strips together, that of one strip being unity.
90	49	1.81
57	81	1.85
30	14	1.70
17	9	1.57
13	7	1.60
4	2.1	1.34
$1\frac{3}{4}$	0.9	1.15

The discrepancies between parts of Tables I. and II. are to be accounted for by the adoption of a different arrangement of connecting wires in the two sets of experiments. The way in which allowance should be made for the capacity of the leads, when this is not very small compared with the capacity to be measured, is at present under investigation, and the above Table can only be taken, therefore, as showing that the capacity of two vertical and parallel wires is not twice that of one wire, unless they are at a distance apart of nearly one-third of their length \*.

Similar experiments were made with two zinc cylinders, the diameter of each cylinder being  $1\frac{1}{2}$  inches, and the length of each cylinder 9 feet  $1\frac{1}{2}$  inches, the capacity of each cylinder taken alone in free space is taken as unity. If these two cylinders were suspended one foot apart in the centre of the large Laboratory above described, and hung vertically, their total capacity only amounted to 1.46 times that of either cylinder taken alone. A further experiment was made with these cylinders. One of them was cut longitudinally and rolled out into a flat strip, and suspended in the same position vertically, the capacity of the original cylinder being taken as unity. The capacity of the sheet when rolled out into a strip was found to be 10 per cent. greater than in its original form.

\* It is clear that the capacity of the object measured, as it would be free in space, is not obtained exactly by deducting that of the leading wire alone from that of the leading wire and object when connected. The assumption that it is so is only a first approximation to the truth.

With the same appliances, a series of experiments was made in the Pender Laboratory on the measurement of the capacity of vertical wires of different diameters. Seven wires of different diameters were suspended vertically by means of silk strings from the ceiling of the Laboratory, and the capacity of each wire was measured separately, a correction being made for the capacity of the terminal, and of course also for the fine wire or lead connecting the wire under experiment with the commutator. The lengths of the wires were about 12 feet in all cases. The following Table shows the result of the measurements, the capacity of the wires being given in micro-microfarads (M.M.Fds.), the fourth column showing the capacity as calculated from the formula

Capacity (in electrostatic units) =  $\frac{1}{2 \log_e l/r}$  where  $l$  is the length of wire and  $r$  is the semi-diameter in centimetres.

TABLE III.—Measurement of Capacity of Wires of various diameters suspended vertically in a large room.

Diameter of wire in inches.	Length of wire in feet.	Mean Value of Capacity in M.M.Fds. observed.	Calculated value by the formula above.	Difference in per cent. between the observed and calculated values.
·0047	11·44	18·79	17·62	6·6
·0075	12·23	21·36	19·59	9·0
·0127	12·29	22·56	20·73	8·8
·0182	12·21	23·76	21·38	11·1
·0278	12·04	24·24	22·06	9·9
·0485	12·33	26·51	23·97	10·6
·1381	12·02	32·36	27·00	19·8

The above formula has been deduced on the assumption that the form of a very long thin wire may be considered as a limiting case of a prolate ellipsoid of revolution. It can be shown that the electrical capacity ( $C$ ) of an ellipsoid of semiaxes  $a$ ,  $b$ , and  $c$  in infinite space is given by the expression \* :

$$\frac{1}{C} = \frac{1}{2} \int_0^\infty \frac{du}{\sqrt{(a^2 + u)(b^2 + u)(c^2 + u)}}.$$

\* See Article *Electricity* by Prof. Chrystal, 9th Edition of the *Encyclopædia Britannica*, vol. viii. p. 30.

If we put  $b=c$  in the above formula, it can be shown that

$$C = \frac{2 \sqrt{a^2 - b^2}}{\log_e \frac{a + \sqrt{a^2 - b^2}}{a - \sqrt{a^2 - b^2}}}$$

Hence the above expression gives us the capacity of the ellipsoid of revolution.

If the ellipsoid is very elongated so that  $b$  is very small compared with  $a$ , then if  $e$  is the eccentricity of the principal elliptical section,  $e$  is nearly equal to unity, and  $1+e$  is nearly equal to 2.

Hence  $(1+e)(1-e) = 2(1-e)$  nearly  
and  $a(1-e^2) = 2a(1-e)$  nearly.

Accordingly, since  $\sqrt{a^2 - b^2} = ae$ , we can say that

$$a - \sqrt{a^2 - b^2} = b^2/2a \text{ nearly,}$$

and  $\log_e \frac{a + \sqrt{a^2 - b^2}}{a - \sqrt{a^2 - b^2}} = 2 \log_e 2a/b$ .

Therefore the capacity of a very elongated ellipsoid of revolution of which  $a$  is the major and  $b$  the minor semiaxis is given by

$$C = \frac{2a}{2 \log_e 2a/b}.$$

If therefore we can consider a thin circular-sectioned wire of diameter  $d$  and length  $l$  as an ellipsoid, we have its capacity in electrostatic units given by the formula

$$C \text{ (in E.S. units)} = \frac{l}{2 \log_e 2l/d},$$

where  $l$  and  $d$  are of course measured in centimetres. To reduce a capacity expressed in electrostatic units to microfarads we have to divide by  $9 \times 10^9$ , and therefore to convert capacity expressed in electrostatic units to the same expressed in micro-microfarads, we have to multiply by  $1\frac{1}{2}$  or to increase by about 11 per cent.

Hence expressed in micro-microfarads the above capacity is:—

$$\begin{aligned} C \text{ (in M.M.Fds.)} &= \frac{l \times 10^6}{2 \times 2.303 \times 9 \times 10^9 \times \log_{10} 2l/d} \\ &= \frac{l}{4.1454 \log_{10} 2l/d}. \end{aligned}$$



An approximate formula for the capacity of a telegraph-wire is also easily found. If an infinitely long filamentary wire is uniformly charged with electricity so that it has  $q$  electrostatic units of charge per centimetre of length, then from the analogy with the case of an infinitely long straight current, it is easy to show that the force due to the filament at any point distant  $r$  centimetres from it, is  $2q/r$ . Hence if the potential at this point is  $V$  we have

$$-\frac{dV}{dr} = \frac{2q}{r}$$

or 
$$V = -2q \log r + Ct,$$

where  $Ct$  is the constant of integration.

If we have two very long straight circular-sectioned wires suspended in air parallel to one another, at a distance  $D$ , the diameter of each wire being  $2r$ , and  $r/D$  being a small quantity, then it is easy to calculate the capacity of the condenser formed of these wires, if we assume them to be so far apart that the electrical charge on each remains uniformly distributed round the surface of each wire. Let one wire be called  $A$ , and let it be positively charged, and the other be  $B$ , and negatively charged. Let  $V_A$  and  $V_B$  be the potentials of these wires, and let the charge on each be  $q$  electrostatic units per centimetre of length, then their capacity per unit of length ( $c$ ) is equal to  $q/(V_A - V_B)$ .

Now from the expression for the potential of the electrified filament we see that

$$V_A = (-2q \log r + Ct) - (-2q \log D + Ct),$$

$$V_B = -(-2q \log r + Ct) + (-2q \log D + Ct),$$

$$V_A - V_B = 4q(\log D - \log r) = 4q \log D/r.$$

The capacity per unit of length is therefore given by

$$c = \frac{1}{4 \log D/r} \text{ (in electrostatic units).}$$

If we employ ordinary logarithms and express the capacity per unit of length in micro-microfarads ( $c'$ ) this becomes

$$\begin{aligned} c' &= \frac{10^6}{4 \times 2.303 \times 9 \times 10^9 \log_{10} D/r} \\ &= \frac{0.1208}{\log_{10} 2D/d}, \end{aligned}$$

where  $d$  is the diameter of either wire, and  $D$  their distance from centre to centre. The formula for the capacity per unit of length of the single telegraph-wire of diameter  $d$  supported at a height  $h$  above the earth, is easily deduced from the above. For since the ground-surface must be a zero-potential surface, the capacity  $c$  in electrostatic units of the single wire per unit of length under these conditions must be

$$c = \frac{2}{4 \log_e 2D/d} = \frac{1}{2 \log_e 4h/d},$$

and the capacity  $c'$  per unit of length in micro-microfarads will be

$$\begin{aligned} c' &= \frac{10^6}{2 \times 2.303 \times 9 \times 10^9 \log_{10} 4h/d} \\ &= \frac{0.2415}{\log_{10} 4h/d} \text{ (in M.M.Fds.)}. \end{aligned}$$

Accordingly the capacity  $C$  of a telegraph wire  $l$  centimetres long and  $d$  centimetres in diameter, and at a height  $h$  centimetres above earth, is given in micro-microfarads by the formula

$$C = \frac{0.2415l}{\log_{10} 4h/d} \text{ (M.M.Fds.)}$$

or very nearly by

$$C = \frac{l}{4 \log_{10} 4h/d} \text{ (M.M.Fds.)}.$$

To test this last formula, an experiment was made in the open air with a long wire held parallel to the earth's surface, on insulators at a height of about six feet above the ground. The length of this wire was 500 feet or 15,240 cms. The height of the wire above the ground was 6 feet or 183 cms., and the diameter of the wire was .0645 inch, or 0.164 cm. The observed value of the capacity of this wire *in situ* was 1081 micro-microfarads. The value of the capacity calculated from the formula

$$C \text{ (in M.M.Fds.)} = \frac{0.2415l}{\log_{10} 4h/d}$$

is nearly 1000 micro-microfarads, the difference between this calculated and the observed value being about 8 per cent.

In the same manner the capacity of a vertical wire was measured in the open air, and compared with the theoretical value as given by calculation. In this case the length of the wire was 111 feet, or 3385 cms., and the diameter of the wire was 0.085 inch, or 0.215 cm. The observed value of this wire when suspended vertically in the air with the bottom end about six feet from the ground, is 205 micro-microfarads. The value calculated by the formula

$$C \text{ (in M.M.Fds.)} = \frac{l}{4.1454 \log_{10} 2l/d}$$

is 181 micro-microfarads. The observed value is again greater than the calculated value by about 10 per cent.

It will thus be seen that in all these cases the observed value of the capacity of the wire, whether vertical or horizontal, appears to come out, roughly speaking, about 10 per cent. greater than the calculated value. Approximately, the same difference was found in the case of the capacity of a zinc disk suspended in the Pender Laboratory. The disk was made of sheet zinc circular in form, and 60 inches in diameter. The calculated capacity of this disk in free space is 48.1 electrostatic units, or 53.44 micro-microfarads\*. The measured capacity in micro-microfarads was found to be 59.95, the difference being about 12 per cent. In all these cases, except that of the horizontal wire, the differences between the observed and the calculated values appear to depend upon the proximity of neighbouring objects or the ground, and upon the way in which connexion is made to the commutator. The capacity of a body together with that of the connecting wire is not, strictly speaking, the sum of the separate capacities of the body and the wire measured *in situ*. In an experiment with one of the iron strips, an apparent decrease of 5 per cent. in the capacity was found when the connexion was changed from the bottom to near the middle. The mathematical formula

\* The capacity of a thin circular disk when insulated in infinite space is numerically equal to  $d/\pi$  in electrostatic units, where  $d$  is the diameter of the disk in centimetres.

gives us the value of the capacity of the body in infinite space, but its measured capacity is in practice its capacity relatively to earth and depends on two things :—the proximity of neighbouring earth-connected bodies, and the manner of attachment to the measuring device. The first always increases the capacity above the calculated value, while the second decreases it. It appears that the net result in the case of the capacity of a disk of about five feet in diameter, when insulated and hung up in the middle of a room 40 feet long, 18 feet high, and 30 feet wide, with the connexion taken away from the bottom edge, is numerically in excess of its calculated or theoretical capacity in free space by about 10 or 12 per cent.

Another interesting experiment was tried on the relative capacity of two lengths of No. 30 copper wire, each 12 feet long. One of them was preserved straight and suspended vertically in the Laboratory as above described ; the other was bent into a spiral about 2 inches in diameter, and 6 feet in length over all, and then again into a closer spiral  $\frac{1}{4}$  inch in diameter, and 18 inches in length over all. Taking the capacity of the straight wire as unity, the capacity of the long coil of large diameter was 0·8, and the capacity of the short coil of small diameter was 0·32, showing how much the capacity of a wire of given length is decreased by coiling it into a spiral.

One of the uses to which the above-described commutator can be put is that of determining the capacity of leyden-jars in absolute measure ; at any rate, the capacity corresponding to frequencies in the neighbourhood of 100. Instrument-makers still retain the absurd custom of speaking of leyden-jars as pint, quart, and gallon sizes, instead of marking on them their capacity in absolute measure. Now that leyden-jars are so much used in wireless telegraphy, the necessity often arises for knowing their approximate absolute capacity, and it is much to be desired that instrument-makers should forsake the custom of denominating their different leyden-jars in the present manner.

Incidentally, the apparatus may be used for more or less accurate determinations of the electromagnetic constant “ $v$ ”.

One method by which a small capacity of known value can be made with a fair amount of accuracy is as follows :—Two cylindrical air condensers are constructed, each of which consists of a cylindrical rod or thick-walled tube placed in the interior of another concentric tube. Two condensers of this kind are prepared, one about double the length of the other ; one may be, say, a foot long, and the other two feet long. The tubes may be of the quality known as “triblet-drawn” brass tube, one exceeding the other in diameter by about 2 millimetres. These tubes may then be cut up into the requisite lengths. The ellipticity and variation of diameter in length of such tubes are very small indeed.

These pairs of tubes can then be formed into two air condensers by fixing the inner tube concentrically within the outer tube by means of ebonite disks at the end. By the adoption of known mechanical methods, the concentric adjustment of the tubes can be made very accurately, and the radial thickness of the air space determined. In this manner two cylindrical air condensers can be constructed identical in every way, except that they differ in length.

If  $c$  is the capacity per unit of length of the middle part of the condenser, where the strain-lines are truly radial, and if  $L$  is the length of the condenser, then the capacity  $C$  of the condenser is expressed by a function of the form  $C = x + cL$ , where  $x$  is an unknown quantity depending on the distribution of the electric strain at the ends of the tubes. Hence if we measure the capacity of the above two condensers by means of the rotating commutator, and take the difference of these capacities, this is the value of the capacity of a length equal to the difference of the lengths of the condensers, and therefore the capacity per unit of length of one of these condensers is known, disregarding the uncertain distribution of the strain-lines at the ends. If the device of employing a guard-ring or guard-tube is adopted, then the capacity of the inner portion of such a cylindrical guard-tube condenser cannot be determined simply by charging and discharging that inner portion through a galvanometer, without at the same time charging and discharging the guard-tubes through a by-path, or else redistributions of electricity take place at each

discharge, which vitiate the result. This source of error was pointed out and guarded against by Prof. J. J. Thomson (1883) and by Prof. J. J. Thomson and Mr. Searle (1890) in making this class of measurement.

*Measurement of Inductance.*—If two such commutators as we have described were mounted on the same spindle, with the eight radial teeth of each centre wheel (I in fig. 1) insulated from each other, and a second central brush added in the correct relative position to the first, we should obtain an instrument similar in principle to the secohmmeter of Professors Ayrton and Perry; but we have thought it worth while, in order to get a simpler apparatus, to sacrifice reversibility and construct simply a double contact-breaker on the same lines. By making the apparatus substantial and eliminating all insulating material, except air, from the rotating drums, and abolishing all flimsy spring-contacts, we have constructed an instrument which is much more satisfactory to work with than the secohmmeter as made by the ordinary instrument-maker (Pl. VI. fig. 5). This double contact-breaker consists of a steel shaft which carries on it two circuit-interruptors constructed in the following manner:—Each of these consists of two wheels, like crown wheels, having four teeth, and these two wheels are set on insulating bushes with the teeth of one wheel interspaced between those of the other. The shaft carries two such barrels (see fig. 5), and the developed surface of these barrels is shown in fig. 6. The barrels are formed of gun-metal, and against each barrel press two brass gauze brushes carried on insulated brush-holders. One brush bears on the continuous flange of one part of each barrel, and the other brush alternately makes and breaks contact with it by bearing on that part of the barrel occupied by the interlocked teeth. The two barrels can be set relatively to one another in any position on the shaft. These two barrels serve the purpose of making and breaking two separate electric circuits in such fashion that at the moment when one circuit is being broken, the other is complete, and at the moment when the first circuit is being completed, the other is broken. The arrangement is direct-driven through a flexible coupling by a one-sixth H.P. direct-current shunt motor.

In the measurement of inductance this double interruptor is employed like the secohmmeter of Professors Ayrton and Perry. The coil of which the inductance is to be determined is balanced on a Wheatstone-bridge, and the two interruptors of the rotating appliance are inserted respectively in the battery and galvanometer circuits, so that if the apparatus is set rotating after the steady balance of the non-inductive resistance on the bridge has been obtained, it will eliminate every alternate inductive electromotive force due to the inductance of the coil, and cause the galvanometer to give a steady deflexion. To evaluate this inductance in absolute measure, we prefer the method described by Professor A. Anderson\*. In this method a variable resistance  $r$  is placed in the bridge circuit in series with the galvanometer connected to a Wheatstone-bridge, and a condenser of known capacity  $C$  is joined in, as shown in the diagram (see fig. 7), and the double interruptor inserted in the battery and galvanometer circuits. When the steady or ohmic resistance of the inductive coil has been determined in the usual manner, the interruptor is set in rotation, and the value of the resistance  $r$  in series with the galvanometer is altered until the galvanometer deflexion vanishes. This last change does not upset the adjustment of the arms of the bridge already made in obtaining the ohmic resistance of the coil. If  $P$ ,  $Q$ ,  $S$  are the arms of the bridge, and  $R$  is the ohmic resistance of the coil under test, of which the inductance is  $L$ , then the ohmic resistance  $R$  and inductance  $L$  of the coil are given by the equation

$$R = PS/Q,$$

$$L = C\{r(R + S) + RQ\} \dagger.$$

Fig. 7 shows the galvanometer and battery connected to a change-over switch  $mm$  in order that they may be placed relatively to the four arms of the bridge in the position giving the most sensitive arrangement for the resistances

\* See Phil. Mag. vol. xxxi. p. 329 (1891); or 'The Electrician,' vol. xxvii. p. 10.

† For the proof of this formula for the inductance, we refer to the original paper by Professor A. Anderson (*loc. cit.*).

employed. We understand that Prof. Stroud has employed one of these arrangements for some time past in the measurement of inductance, but no publication of it appears to have been made prior to that by Prof. Anderson.

This method of measuring inductance by a combination of the double interruptor, with the Anderson method, is one of the most perfectly satisfactory methods that can be employed in the laboratory. It is an absolute method in that it requires no arbitrary standard of inductance, and yet, at the same time, it requires no determination of a speed ; it only assumes the possession of resistance-boxes and a known capacity.

The value of small inductances, such as are best reckoned in millihenrys, can be obtained most accurately by measuring them as the difference of two larger inductances. Thus, for instance, if a coil is given of small inductance, its ohmic resistance is first measured. It is then joined in series with the coil of considerably larger inductance, and the inductance of the two coils together measured as above described. The larger inductance is then determined separately, and the small inductance becomes known by the difference. In this manner it is possible to determine with very fair accuracy the inductance of quite small coils of wire.

In conclusion we have pleasure in mentioning the assistance rendered to us in portions of this work by Dr. G. A. Hemsalech, who devoted a considerable amount of time to the experimental work at one stage of the investigation.

#### DISCUSSION.

Prof. AYRTON said he was glad to see that the authors had brought out an apparatus constructed on engineering lines. He mentioned that the secohmmeter used in his laboratory was not the instrument of the instrument-makers' catalogues, but more like the one exhibited. Prof. Fleming had given some account of the history of the subject, and had referred



to early experiments carried out by using tuning-forks as commutators. Rotating commutators were, however, in use some time before the introduction of tuning-fork arrangements. The fact that air was superior to mica, ebonite, or other substances as the insulating material at the surface of a rotating commutator had been recognized by Prof. Perry and himself in a patent taken out many years ago. The authors had raised the question of the legitimacy of subtracting the measured capacity of the commutator and leads from the measured capacity of the commutator, leads, and condenser in order to obtain the capacity of the condenser. He pointed out that the results of the experiments described in the paper showed that this procedure was wrong. He asked in what respect Anderson's method of measuring a self-induction was superior to the method of comparing it directly with a standard variable self-induction. Referring to the galvanometer used in these experiments, Prof. Ayrton pointed out that the device of shunting the magnetic flux through a piece of soft iron had been used before. There were two objects in employing such a shunt. In the first case, when using an ordinary moving-coil galvanometer as a voltmeter, it was necessary to keep the sensibility constant, and any alteration in the strength of the magnets could be counterbalanced by a movement of the shunt. In the second case, the shunt was useful in the construction of differential moving-coil galvanometers. Some years ago a series of observations were conducted in his laboratory to determine the errors which might enter into experiments carried out with a rotating commutator, and he remarked that, in order to avoid contact differences of potential, it was essential that the commutator and the brushes should be made of the same material.

Prof. S. P. THOMPSON said the experiments were the first which had been made upon the capacities of wires suspended near each other in air. Referring to the measurement of small capacities, Prof. Thompson briefly described a method which he had published similar to Carey Foster's method of comparing two nearly equal resistances. All that is required

for accuracy is a known standard capacity and a calibrated sliding condenser.

Mr. A. CAMPBELL exhibited the commutator used for condenser tests at the National Physical Laboratory. It is similar to that designed by Mr. Searle and used by him and Prof. J. J. Thomson in their determination of the value of " $\epsilon$ ." In this commutator the ebonite insulation does not fill the spaces between the segments, and is never touched by the brushes, thus giving satisfactory insulation. By its aid many measurements have been made of the B.A. air-condensers, the capacity of each of these being about 0.02 m.f.d. The galvanometer used was so sensitive that the time-measurement had to be carefully performed to get equal accuracy. In the earlier experiments an ordinary moving magnet galvanometer was used, but it was discovered that if the magnet at its zero position was not exactly parallel to the planes of the coils, considerable changes occurred in the observed capacities when the battery was reversed. This effect was due to the fact that, with the needle in such a position, the galvanometer could respond to alternating currents, and that its deflection (except when the needle was exactly at right angles to the coil-axis) was partly due to the mean current and partly to the square-root mean-square current. When a condenser of  $\frac{1}{3}$  m.f.d. was put in parallel with the galvanometer the effect practically disappeared. A moving-coil galvanometer, however, was found to be quite free from such effects, and this type had been used in nearly all the tests. The differential galvanometer described by the authors appeared admirable, and would be a useful instrument for a number of purposes, a great advantage being that the mutual inductance from coil to coil would be very small.

Mr. JACOB asked Mr. Campbell if he was sure that the movement of the galvanometer-needle mentioned by him was not due to electrostatic effects. He pointed out that if a differential moving coil-galvanometer was correctly balanced for one point of the scale, it did not follow that it would remain balanced at any other point. It was a matter of

common knowledge that the total capacity of wires near each other was less than the sum of the capacities of the wires taken separately.

Mr. J. T. MORRIS asked if the authors had any proof that the condenser was perfectly charged and discharged on every occasion. He drew attention to the fact that the capacity might depend upon the form of the wave of potential difference which charged it.

Mr. R. APPELYARD said that the capacity of a condenser with mica dielectric determined from a single charge and discharge was practically the same as that obtained from several charges and discharges per second. This was not the case with rubber. He asked if the authors had observed differences in capacity depending upon the point of attachment of the leading wire.

Mr. W. C. CLINTON, in reply, said they had used Anderson's method because they found it more convenient than any other. It required no arbitrary standard of inductance or determination of speed, the only things required being resistance-boxes and a known capacity. They had obtained different capacities for wires by varying the point of attachment of the lead, the maximum variation amounting to about 5 per cent of the total capacity.

XXXVII. *On the Thickness of the Liquid Film formed by Condensation at the Surface of a Solid.* By Dr. G. J. PARKS\*.

It was known more than half a century ago † that when a solid is placed in a gas or vapour there is a condensation of the latter on the surface of the solid, and in particular that glass has the power of condensing water-vapour at temperatures above the dew-point.

Arago ‡ proposed to measure the amount of condensation by the optical method of interference, and quite recently Lord Kelvin § has suggested a method depending upon electrical conductivity.

In almost every department of physical research glass bulbs or tubes are used, and the presence of moisture on the surface of the glass is a continual source of trouble. Prof. J. Trowbridge || has lately called attention to this matter in connexion with spectrum analysis.

There can be little doubt also that many of the standard results for the specific heats of finely divided or porous solids are incorrect, for if a solid is perfectly dry, heat will be evolved on wetting it ¶ when it is placed in the calorimeter, and if it is not dry then the specific heat obtained is not the true specific heat of the solid; in either case the specific heat obtained will be too high. Thus, from the most recent determination of the specific heat of pure precipitated silica, well dried and sealed in a bulb, the value appears to be  $\cdot 1808^{**}$ , but the values previously obtained for amorphous silica are much higher than this.

The present brief inquiry, which is not intended to be by any means exhaustive of the subject, arose out of another

\* Read February 27, 1903.

† Jamin et Bertrand, *Phil. Mag.* [4] vi. p. 157 (1853); *Comptes Rendus*, June 1853, p. 994.

‡ See *Phil. Mag.* [4] vi. p. 157 (1853).

§ Lord Kelvin, *Phil. Mag.* [6] iv. p. 181 (1902).

|| Trowbridge, *Phil. Mag.* [6] iv. p. 156 (1902).

¶ Parks, *Phil. Mag.* [6] iv. pp. 240, 251 (1902).

\*\* Bellati e Finazzi, *Atti del R. Istituto Veneto*, Tomo lxi. Parte Seconda, p. 567 (1902).

investigation, not yet completed, in which the author has attempted to determine by direct experiment the surface-pressure of water and other liquids in contact with glass.

It was found that everything depended on keeping the surface of the glass perfectly free from moisture until the moment of the experiment; and the author was thus led to consider the quantity of moisture concerned in surface-pressure, in the Pouillet effect, and in surface-action generally.

In the first experiment some cotton silicate, similar to that used in the author's previous investigation\*, was packed tightly into a test-tube and the mouth of the tube was drawn out to a fine neck, but not sealed.

The weight of the silicate was 3.37 grammes, the average diameter of the cylindrical filaments was .00175 cm., the sp. gr. was 2.7, and the estimated area of surface was 847 sq. cm. per gm.

Hence the superficial area of the silicate was  $3.37 \times 847 = 2854$  sq. cm., and allowing for the area of surface of the test-tube, the whole area of glass surface amounted to about 2900 sq. cm.

The tube was placed in an open beaker, and this was covered with a large inverted beaker standing over some water in a shallow tray and kept in a closed glass cupboard at nearly constant temperature.

The vapour which filled the chamber slowly diffused into the test-tube through the narrow aperture, and became condensed on the surface of the glass. The experiment continued for 16 days, the tube being weighed at intervals. The outside of the tube was wiped with a clean cloth before

Time.	Weight of tube and silicate.	Increase of Weight.	Estimated thickness of film (cm.).
12 hours .....	9.3602	.0200	$6.9 \times 10^{-6}$
1 day .....	9.3644	.0242	$8.3 \times 10^{-6}$
2 days .....	9.3672	.0270	$9.3 \times 10^{-6}$
4 " .....	9.3710	.0308	$10.6 \times 10^{-6}$
10 " .....	9.3774	.0372	$12.8 \times 10^{-6}$
15 " .....	9.3790	.0388	$13.4 \times 10^{-6}$
16 " .....	9.3790	.0388	$13.4 \times 10^{-6}$

\* Phil. Mag. [6] iv. p. 246 (1902).

each weighing, so that the observed increase of weight was entirely due to condensation by surface-action. The temperature never varied much from  $15^{\circ}\text{C}$ . The above table shows the results of the various weighings and the estimated thickness of the film of moisture. The initial weight of the tube and silicate when dry was 9.3402 grammes.

In another experiment the silicate was placed loosely in the tube and the mouth of the tube was allowed to remain at its ordinary width, about 1.5 cm. The experiment was made much more quickly than the first one, but the final result was the same.

Temperature during experiment about  $12^{\circ}\text{C}$ .

Weight of silicate 1.10 gm.

Total area of surface of silicate and tube about 1000 sq. cm.

Initial weight of tube and silicate 7.9517 gm.

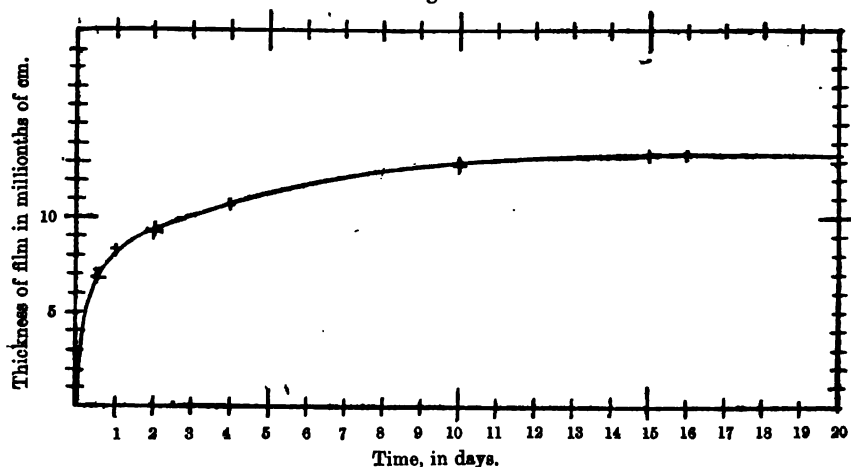
Weight after 4 days 7.9650 gm.

" 6 " 7.9650 "

Increase of weight .0133 "

Estimated thickness of film  $13.3 \times 10^{-6}$  cm.

Fig. 1.



The cotton silicate thus covered with a film of moisture showed no alteration in appearance even when examined under the highest power of the microscope, but when the

silicate was placed in water no heat was evolved, though when the same substance was thoroughly dried and placed in water the heat evolved amounted to  $\cdot 0011$  calorie per sq. cm. Hence it may be inferred that the Pouillet effect for water in contact with glass at  $12^{\circ}$  C. is confined to a film of moisture the thickness of which is about  $13\cdot 3 \times 10^{-6}$  cm.

It will be interesting to compare with this result the results obtained by other experimenters with different substances and under widely different conditions. The earliest measurement of surface condensation of which the author has been able to find an account, is that of Magnus\*, who, from experiments on the expansion of sulphurous acid gas, found that the amount of gas condensed on the surface of smooth glass rods was  $\cdot 0008$  cub. mm. per sq. mm., that is  $80 \times 10^{-6}$  cub. cm. per sq. cm. of surface.

It is not improbable that in these experiments the sulphur dioxide was condensed by chemical combination with a film of water previously existing on the surface of the glass, but it may be noticed that the result obtained is of the same order of magnitude as all the other results quoted in this paper.

Martini† found that some precipitated silica exposed to aqueous vapour increased in weight by 80 per cent. without any alteration in appearance; on putting this moist silica into water no heat was evolved, though the heat evolved on wetting the dry silica amounted to 19 calories per gramme. Martini does not state the area of surface exposed by the powder, but the author has shown‡ that when dry silica is wetted, the amount of heat evolved is about  $\cdot 00105$  calorie per sq. cm.; and hence we may take the area of surface of the powder used by Martini as about 18,000 sq. cm. per gm., and the extreme thickness of the aqueous film would therefore be  $\frac{\cdot 8}{18000} = 4\frac{1}{2} \times 10^{-6}$  cm.

It should be remarked here that when a powder is exposed for a long time in an open tray it is likely to receive some

\* Magnus, *Phil. Mag.* [4] vi. p. 336 (1853).

† Martini, *Atti del R. Istituto Veneto*, Tomo lix. Parte Seconda, p. 624 (1900).

‡ *Phil. Mag.* [6] iv. p. 247 (1902).

moisture by the ordinary process of condensation at temperatures below the dew-point, and thus the more exposed portions of the powder may receive excess of moisture.

Bellati and Finazzi\* have recently made an excellent series of experiments showing the relation between the amount of moisture absorbed by silica and the heat evolved on putting the powder into water. The area of surface exposed by the silica is not stated, but the authors consider with good reason that if the powder were perfectly dry the heat evolved on wetting it would amount to 26 calories per gm., and hence we may assume the surface exposed by the powder to amount to about 25,000 sq. cm. per. gm.

In the following table the figures of the first two columns have been selected from the original paper referred to, and the other three columns have been introduced by the author

Parts of moisture absorbed by 100 parts of dry silica. (a)	Heat evolved per gramme of silica. (q)	Reduction of the heat evolved by previous absorption of moisture. (26-q)	Thickness of water film $\frac{10^6 \cdot a}{25000}$	Heat evolved per sq. cm. by a film of this thickness $26-q$ $\frac{25000}{25000}$
2.38	18.29	7.71	$95 \times 10^{-6}$	$3.08 \times 10^{-4}$
5.35	12.23	13.77	$2.14 \times 10^{-6}$	$5.51 \times 10^{-4}$
8.59	9.17	16.83	$3.44 \times 10^{-6}$	$6.73 \times 10^{-4}$
12.92	7.61	18.39	$5.17 \times 10^{-6}$	$7.36 \times 10^{-4}$
18.83	6.50	19.50	$7.53 \times 10^{-6}$	$7.80 \times 10^{-4}$
27.36	5.25	20.75	$10.94 \times 10^{-6}$	$8.30 \times 10^{-4}$
39.95	3.70	22.30	$15.98 \times 10^{-6}$	$8.92 \times 10^{-4}$
46.35	2.94	23.06	$18.54 \times 10^{-6}$	$9.22 \times 10^{-4}$
56.48	1.66	24.34	$22.59 \times 10^{-6}$	$9.74 \times 10^{-4}$
64.78	.90	25.10	$25.91 \times 10^{-6}$	$10.04 \times 10^{-4}$
76.94	.19	25.81	$30.78 \times 10^{-6}$	$10.32 \times 10^{-4}$

for the purposes of the present inquiry. An example will be sufficient to explain the table and the diagram. When the dry silica has absorbed, say, 2.38 per cent. of moisture it is put into water and the heat evolved is found to be 18.29 calories per gm.

But if the silica had been perfectly dry the heat evolved would have been 26 calories, hence the heat due to 2.38 per

\* Bellati e Finazzi, *Atti del R. Istituto Veneto*, Tomo lxi. Parte Seconda, p. 514 (1902).



cent. of moisture must have been  $26 - 18.29 = 7.71$  calories per gm. .

The thickness of the film of moisture is about

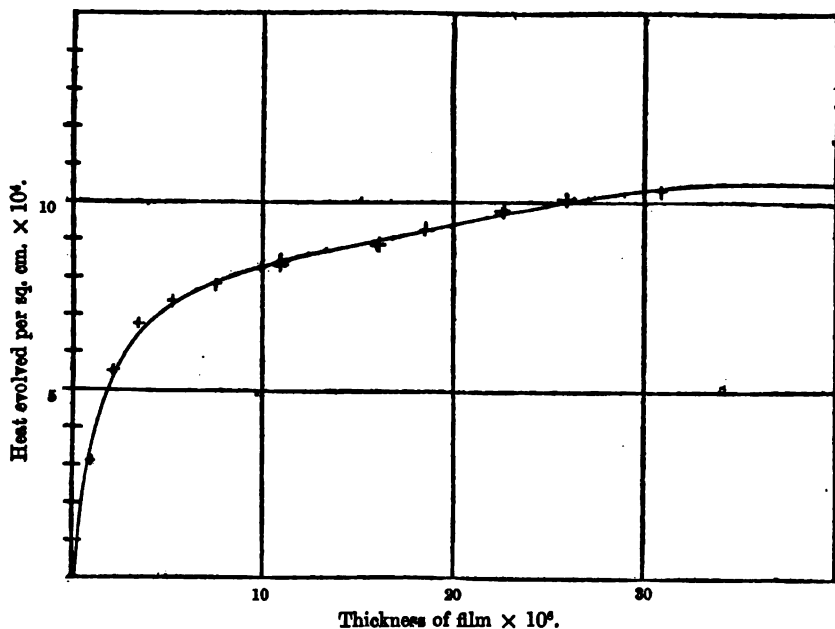
$$\frac{.0238}{25000} = .95 \times 10^{-6},$$

and the corresponding amount of heat per sq. cm. is

$$\frac{7.71}{25000} = 3.08 \times 10^{-4} \text{ calories.}$$

The results show that when the water film is only one millionth of a centimetre in thickness, the heat evolved is

Fig. 2.



about one third of the whole amount, when the thickness of film is two millionths the heat evolved is about one half of the whole, and on further increasing the thickness of the film the amount of heat evolved slowly approaches a maximum which it reaches when the thickness is about  $31.6 \times 10^{-6}$ , the heat evolved being then .00105 cal. per sq. cm.

Dr. C. Barus\* gives some valuable data on the size of the water particles produced by condensation on a solid nucleus. In the experiments described it seems that the condensation must in the first place be caused by the surface action of the nucleus, though as the exhaustion of the chamber proceeds the average size of the water particles increases by ordinary condensation at temperatures below the dew-point. If we subtract the average diameter of the nuclei from the average diameter of the drops, and halve the remainder, this will give the thickness of the film of water.

In the following table the first two columns have been taken from the original paper of Dr. Barus, and the last column has been inserted by the present writer. The results for the first six exhaustions only have been selected.

Diameter of nucleus  $260 \times 10^{-6}$  cm.

Number of exhaustions.	Diameter of water particle.	Thickness of film.
1 .....	$280 \times 10^{-6}$	$10 \times 10^{-6}$
2 .....	$310 \times 10^{-6}$	$25 \times 10^{-6}$
3 .....	$330 \times 10^{-6}$	$35 \times 10^{-6}$
4 .....	$360 \times 10^{-6}$	$50 \times 10^{-6}$
5 .....	$390 \times 10^{-6}$	$65 \times 10^{-6}$
6 .....	$420 \times 10^{-6}$	$80 \times 10^{-6}$
Diameter of nucleus $360 \times 10^{-6}$ cm.		
1 .....	$370 \times 10^{-6}$	$5 \times 10^{-6}$
2 .....	$390 \times 10^{-6}$	$15 \times 10^{-6}$
3 .....	$410 \times 10^{-6}$	$25 \times 10^{-6}$
4 .....	$420 \times 10^{-6}$	$30 \times 10^{-6}$
5 .....	$440 \times 10^{-6}$	$40 \times 10^{-6}$
6 .....	$460 \times 10^{-6}$	$50 \times 10^{-6}$

Dr. Barus remarks that "the use of Kelvin's vapour-tension equation breaks down quantitatively for the present purposes in practice." The reason for this will be clear when it is remembered that Kelvin's vapour-tension equation is only intended to apply to a condition of equilibrium existing between a liquid and its vapour; but in condensation upon solid surfaces another element must be taken account

\* Barus, Phil. Mag. [6] iv. pp. 24 to 29 and pp. 262 to 269 (1902).

of, viz., a force of the nature of an attraction between the solid and the liquid or vapour, which causes a pressure, probably a very great pressure, in the liquid at the surface of the solid. The author hopes to be able at some future time to give the numerical values of this surface pressure for various liquids in contact with glass.

It now appears that in all cases where condensation of moisture takes place at a solid surface, and at temperatures not below the dew-point, the thickness of the surface film varies from  $10 \times 10^{-6}$  to  $80 \times 10^{-6}$  cm. according to the substances used and the conditions of temperature and pressure, and for the water film on glass in saturated vapour at  $15^{\circ}$  C. the thickness is about  $18.4 \times 10^{-6}$  cm.

According to Prof. J. J. Thomson \* the mean radius of the drops formed by condensation in electrified gas is of the same order of magnitude, being  $81 \times 10^{-6}$  cm. for negatively electrified oxygen, and  $68 \times 10^{-6}$  cm. for positively electrified oxygen; the size of the nucleus is not known, but it is probably very small.

H.M. Dockyard School, Portsmouth.  
November 1902.

#### DISCUSSION.

Prof. EVERETT remarked that similar experiments upon different kinds of glass had been carried out by Kohlrausch. The glass, in the form of powder, was placed in a platinum dish under a bell-jar exposed to water vapour. The increases in weight varied from 2 per cent. to 18 per cent., whereas the increase observed by Dr. Parks was only 1.2 per cent.

Prof. S. P. THOMPSON congratulated the Author upon the results of his experiments, but advised him to be cautious in using them in any attempt to determine the law of molecular attraction. Similar experiments were carried out in Bunsen's laboratory about twenty years ago.

Dr. J. A. HARKER said that the liquid film on the surface of glass or porcelain was often a source of trouble in high-temperature gas-thermometry. He had found that in exhausting Röntgen-ray tubes it was apparently possible to get a complete vacuum at about  $300^{\circ}$  C., but on heating to a

\* J. J. Thomson, 'The Discharge of Electricity through Gases' (1900).

slightly higher temperature gases were suddenly given off from the walls of the tube.

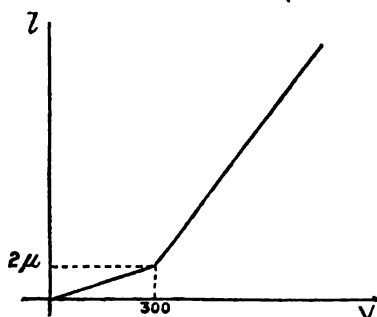
Mr. J. BROWN (communicated).—The examination of an advance proof of the most interesting and suggestive paper by Dr. Parks recalls an investigation of my own, undertaken with a quite different object, viz. the question as to whether the condensed films on plates of copper and zinc could be brought into contact so as to form the electrolyte of a voltaic cell and produce a current. Incidentally I measured very roughly the limit of separation of the plates at which this current ceased. The experiment is described in my paper on "A Theory of Voltaic Action," Proc. Roy. Soc. vol. xli. p. 308 (1886), and as therein stated the apparatus, though well suited to test for the current, was for reasons given not at all fitted for accurate measurements of the film thickness. It would therefore be impertinent to base on such observations any criticism of the thickness of the film measured by Dr. Parks further than to suggest that if the much greater thickness that I should have estimated, or rather guessed from my observations, be at all near the truth it is possible that the electrically conducting film has a much less specific gravity than that of ordinary water.

Also it seems interesting to point out that with apparatus properly designed for the purpose such direct measurement may be possible.

Dr. P. E. SLAW (communicated).—In Dr. Parks' experiments and in all those he quotes, except possibly those of Magnus, the radius of curvature of the solid surface is small, and is in fact comparable with the thickness of the film deposited on it. Perhaps Dr. Parks would try the effect on flat surfaces, *e.g.* the thin iridescent glass obtained when a glass bulb is overblown. It would also be of interest to try what happens below  $0^{\circ}\text{C}$ . Years ago I came across this film on wires of radius about  $\frac{1}{4}$  mm. In Phil. Mag. March 1901, I showed that two wires, crossing at right angles, if brought into contact adhere with a force of the order of 1 dyne, which can be proved due to the capillary action of the film between them.

There was a paper by Mr. Earhart (Phil. Mag. Jan. 1901) on the voltages required for sparking between surfaces when the distance between them is small. The curves

showing the relation of  $V$  to  $l$  consist of two straight lines joined by a very pronounced "knee," corresponding to a sparking distance of between 2 and 4 micra (see sketch). Thus the



ratio  $\frac{dV}{dl}$  suddenly changes when the distance is about  $2\mu$ .

Dr. Parks puts  $0.8\mu$  as the upper limit for the thickness of the film. Suppose two surfaces (in this case large spheres) approach one another to a distance  $2\mu$ —then deducting  $0.8\mu$  for the film on each surface, we have an air-distance of only  $0.4\mu$ . This would be easily bridged by the small vibrations of the apparatus, and probably the bridge of water would be stable. Thus it would happen that the sparking would occur through film only, instead of through air and film, with the results observed. The dust particles in air have their enclosing film of water, say  $0.4\mu$  thick; this film is deep enough to contain and foster any of the well-known *bacilli*, whose smallest dimensions are say  $\frac{1}{3}$  micron. I take it that this film is the habitat, when apart from a host, of all bacteria. This accords with the well-known fact that microbes are unknown in polar regions, where the film would be frozen.

Dr. R. T. GLAZEBROOK said the results were of particular interest to him, because he was at present engaged in making mercury standards of resistance. In his experiments it was necessary to measure the radii of the tubes with an accuracy comparable with the thickness of the liquid film.

Dr. PARKS, in reply to Dr. Harker, said that powdered silica might be heated to nearly  $300^\circ$ , and appear quite dry. On heating it slightly higher, however, large numbers of bubbles were given off suddenly, and the powder resembled a boiling liquid.

XXXVIII. *On an Oscillating Table for Determining Moments of Inertia.* By W. H. DERRIMAN, B.Sc., Demonstrator in Physics, University College, Liverpool\*.

THE following description of an oscillating table for determining moments of inertia is given in the hope that the apparatus may prove useful in the laboratory, both for determining moments of inertia of bodies experimentally, and also for illustrating some of the laws relating to moments of inertia.

With this apparatus the moment of inertia of a body can be determined not only for axes which do, but also for axes which do not pass through the centre of gravity of the body.

If a body of moment of inertia  $I$  is suspended by a wire and allowed to make torsional vibrations, the time of vibration,  $t$ , is given by the formula

$$t = 2\pi \sqrt{\frac{I}{c}},$$

where  $c$  is a constant depending on the dimensions and nature of the material of the wire. This gives the well-known means of determining the moment of inertia of a body about an axis passing through the centre of gravity of the body, the constant  $c$  being determined by another experiment with a body of known moment of inertia.

The apparatus which it is the object of this paper to describe consists of a circular wooden table TT supported by brass rods RRR, to which the suspending wire W is attached by a small vice V. In the diagrams shown, fig. 1 represents a side view of the table, and fig. 2 a plan of the top of the table. P is a pointer attached to the centre of the table, and below is a fixed pointer P' resting on a table beneath. In the top of the table a circular groove (fig. 2) is cut, in which small pieces of lead LLL can slide. These pieces of lead form together half of a circular ring of rectangular cross-section. In setting up the apparatus a plumb-line is first hung from the supporting vice V' and the

\* Read January 23, 1903.

pointer  $P'$  placed immediately below. The plumb-line is then removed and the table suspended by the wire  $W$ . The body whose moment of inertia we require to determine is placed at the given position on the table and the lead weights

Fig. 1.

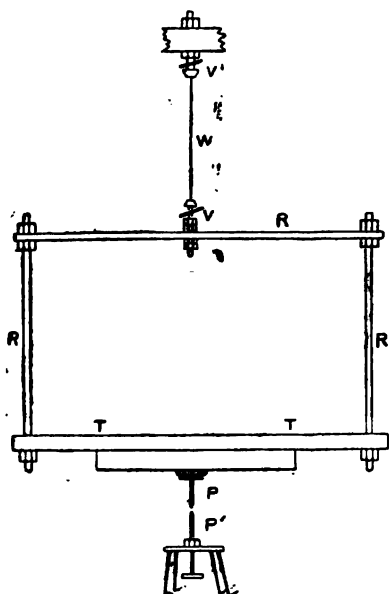
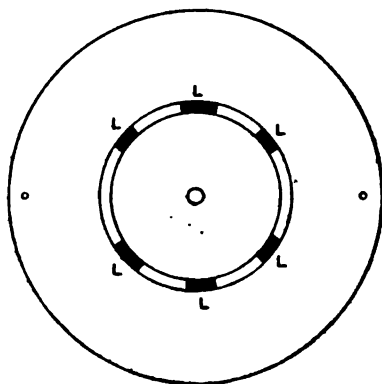


Fig. 2.



LLL moved round in the groove until the centre of gravity of the whole is in the axis  $V/P'$ , this being ascertained by the pointer  $P$  being exactly above  $P'$ . The table therefore always oscillates about the same axis; and since the lead weights are at a fixed distance from this axis, the moment of inertia of the table remains constant. Any alteration of the total moment of inertia is only that due to the body placed on the table.

If the time of vibration of the table alone is observed and then the time of vibration of the table with a body of known moment of inertia placed on it, the moment of inertia of the table can be calculated. It is only necessary then, in determining the moment of inertia of a body about a given axis, to place it on the table in such a position that the given axis

coincides with the fixed axis of vibration, and again determine the time of vibration.

Laws connecting the moments of inertia of a body about different axes can be easily verified with this table, *e. g.*, the law that "the moment of inertia of a body about any axis is equal to its moment of inertia about a parallel axis through its centre of gravity together with the moment of inertia of the whole mass collected at its centre of gravity about the given axis," can be verified by varying the distance of the body from the axis of vibration.

#### DISCUSSION.

Mr. SKINNER described an inertia balance by means of which moments of inertia can be determined without the use of stop-watches. The table which carries the body is suspended by a wire. Fixed to the centre of the bottom of the table there is another wire, similar to the first, but twice as long. This wire carries a screwed brass bar, the axis of the bar being at right angles to the wire. At the middle point of this wire there is a pointer fixed at right angles to it, and on the brass bar are two weights which can be placed at varying distances from the axis. A fourth wire, the same length as the first one, is attached to the bottom of the bar and its lower end is clamped. By arranging so that the upper table oscillates to the left when the bar is oscillating to the right and adjusting the weights on the brass bar until the pointer is stationary, the moments of inertia of bodies placed upon the table can be determined.

Prof. S. P. THOMPSON referred to an inertia table designed by Prof. Perry in which an aluminium ring was supported by a trifilar suspension.



XXXIX. *Exhibition of a Lens.**By* Mr. T. H. BLAKESLEY \*.

THE lens exhibited has the property that the two conjugate foci always move with the same relative rate along the axis. The size of the object always bears to the size of the image the same ratio, so that using the same object the image is always of the same size. The instrument is of one piece of glass, and constitutes a telescope whose magnifying power is the ratio which the object bears to the image in size, linear. The relation of the rate of motion of the object to that of the image is the square of the magnifying power. The following method of construction attains these ends. Let  $D$  be the distance between the centres from which the faces are struck, and let  $l$  be the length of the instrument between the end faces. Then  $l = \mu D$  where  $\mu$  is the index. The quantity  $l - D$  is thus fixed. Divide it into any two parts (algebraically)  $r_1$  and  $-r_2$ , so that  $r_1 - r_2 = l - D$ , and employ these two values  $r_1$  and  $r_2$  as the radii of the end faces. The ratio  $r_1/r_2$  will be the magnifying power  $m$ , which must be interpreted thus:—If the curvatures are towards the same direction  $r_1$  and  $r_2$  have the same sign and  $m$  is positive. Double convexity therefore implies an inversion of the image, or a negative magnifying power. If  $x$  be the distance of the object from the first surface encountered by the light, and  $y$  be the distance of the image from the second surface, both measured positively in the direction opposite to that of light-propagation, then

$$ym^2 - mD = x \text{ where } m = \frac{r_1}{r_2},$$

from which  $\frac{dx}{dy} = m^2$ .

The fundamental condition  $l = \mu D$  is that which implies an infinite focal length for a lens. This condition rules in a telescope in which the principal foci of the objective and ocular coincide. The instrument exhibited has a value  $+5$  for the magnifying power, and was convexo-concave accordingly. One view to take of the instrument is to imagine the space between an objective and ocular properly situated, filled up with glass.

\* Read March 27, 1903.

*XL. Dimensional Analysis of Physical Quantities, and the  
Correlation of Units. By A. F. RAVENSHEAR, B.Sc.\**

CONTENTS.

Introduction : Function of Dimensions and General Indication of  
Conclusions to be established.

I. Conditions giving rise to Dimensional Relations.

II. Dimensions of Mass, Length, and Time.

III. Theoretical Completion of the Correlation of the Units of Dynamical  
Quantities.

IV. One Outcome of Dimensional Analysis may be the Suppression of  
all Qualitative Distinction.

V. Fundamental, Derived, and Secondary Units.

VI. Systems of Dimensions and Remarks on Annexed Tables.

THE use of dimensions underlies all applications of mathematics to physics. Measurements of physical quantities depend on the employment of units of the same kinds as the quantities measured. Such units form the connecting link between the theorems of mathematics and the relations among phenomena which are the especial concern of the physicist. Units which are qualitatively distinct from each other can have no common measure ; they can be correlated only through the medium of dimensions.

In the conventional system of dimensions, the correlation of units is arrested when mass, length, and time are reached. This is no doubt due to the fact that both the physicist and the mathematician agree in regarding mass, length, and time as simple irresolvable data, or ultimate facts, which admit of no analysis. That mass may be regarded as having dimensions has indeed been remarked, but the consequence of this, as regards the theory of the dimensions of physical quantities, do not appear to have been generally recognized. In this paper it will be shown that the usual assumption that because mass, length, and time are ultimates, their units can not be further correlated stands in need of considerable qualification. It will be shown that a further application of the same processes by which different physical quantities are dimensionally analyzed and their units correlated with those of the three

\* Read April 24, 1903.

fundamental quantities, enables these quantities to be further correlated in principle, and their dimensions assigned. Since, however, scientific knowledge is not so complete that the units of all physical quantities can be correlated with those of mass, length, and time, we do not thus arrive at a complete correlation of all units; but while we reduce the list of independent units in one direction, we are led to add to the list any units that can not be correlated with others in the present state of scientific knowledge. This, however, is not the only method of pursuing dimensional analysis, nor is the above result the only possible outcome of such analysis.

At the same time that one outcome of dimensional analysis is a movement down the scale of qualitative distinction towards pure undistinguished quantity, another outcome will be shown to be progress up the scale of qualitative distinction towards a full symbolical description of the physical relations of the phenomenon under consideration. These results may be found to connect together certain diverse opinions on the subject of the significance of dimensional equations, which are occasionally expressed by physicists at the present time. We shall see that dimensional equations in some cases may express physical identity or equivalence, but do not always necessarily do so.

The procedure followed is first to formulate the conditions which give rise to dimensional relations, and then to show how from these the results follow which are here indicated briefly.

### *I. Conditions giving rise to Dimensional Relations.*

Dimensional relations arise in the first instance from quantitative relations among physical phenomena. Such relations are expressed in mathematical language by means of general equations.

1. The first condition is therefore that the quantities must be capable of exact measurement. To be measurable, a quantity must be clearly distinguishable and capable of being divided into parts, and the parts of being joined together without the quantity being thereby affected. This relative independence of parts is necessary in order that the mathematical axioms of quantity may be applied. Cavendish's

attempt\* to compare resistances by leyden-jar discharges may be given as an instance of attempts to measure phenomena which have only imperfectly satisfied this requirement.

2. The second condition is that the phenomena which are measured must be connected by a law of variation. One characteristic of the laws of variation that give rise to dimensional equations is that they must be true without qualification; that is, there must be included in the statement of the law all the conditions upon which its truth depends. Another characteristic is that the conditions included in the statement of the law must be wholly quantitative.

Both these points may be clearly illustrated by asking: What are the dimensions of atomic weight? Avogadro's Law suggests that the dimensions of atomic weight might be those of density. But how are we to introduce into the dimensional equation an allowance for the known exceptions to this law; and how could the condition be introduced that it only holds for substances in the gaseous state? Similar difficulties stand in the way of deducing the dimensions of atomic weight from Dulong and Petit's Law of Atomic Heats. There is the further difficulty also that specific heat appears in this law as an additional factor to be taken into account. Apparently the dimensions of atomic weights can not at present be specified, because their determination is based partly upon such considerations as isomorphism and other analogies which at present, at any rate, are not expressible as quantitative relations.

An examination of other cases in which the dimensions of physical quantities are not known, or in which there is difficulty in assigning them, shows that the reason in those cases also is that no such law is available. Thus the difficulty of assigning the dimensions of the dielectric constants arises because the forces exerted by electric and magnetic charges vary according to some unknown law as we pass from one kind of matter to another. It is obvious, however, on the other hand, that a law which is quantitative, and which includes all the conditions on which its truth depends, can be expressed completely as a mathematical equation.

\* 'Electrical Researches of Cavendish,' Maxwell, p. 637.

3. Equations with numerical coefficients embodying a physical law need not be equally true whatever the magnitudes of the units employed in the measurement of the correlated phenomena. Equations embodying physical laws, can, however, be expressed in a general form with generalized coefficients; and they are then true irrespectively of the magnitudes of the units to which the several quantities entering into them are referred. Such equations, it can be shown, must be homogeneous with regard to some variable or variables which can be independently varied by varying the units. If an equation be made to include quantities of different kinds, which are physically incomparable, it can be shown to break up into as many separate homogeneous equations as there are kinds of quantities, after the manner of equations involving rational and surd quantities, or equations between complex numbers, in pure mathematics. In the following pages quantities which are altered by a change of units are called *changeables* in order to distinguish such alterations from physical variation.

In deriving dimensional formulæ we begin with a measurement of phenomena and the establishment of a quantitative law of variation. The next step is the expression of this law in the form of a mathematical equation by the introduction of a numerical constant. Then we have to satisfy the mathematical requirement of homogeneity. If the law of variation has introduced quantities the dimensions of which have not previously been fixed, the dimensions that will make the equation homogeneous are assigned to them.

Two very divergent views are current as to the interpretation of dimensional equations\*. One of these views is that a dimensional equation expresses physical identity or physical equivalence between the quantity which appears on one side and the complex of mass, length, and time elements which appears on the other side.

The other view is that the dimensional equation merely expresses a law of variation; and that the full meaning of, say, the equation  $[\text{force}] = [M][L][T^{-2}]$  is: The magnitude of the unit of force varies directly as the magnitude of the

\* Discussion on Mr. Williams' Paper on Dimensions, 'Nature,' vol. xlvii. pp. 69, 116.

unit of mass, while the units of length and time remain unaltered ; directly as the magnitude of the unit of length, while the units of mass and time remain unaltered ; and inversely as the square of the change ratio of the unit of time, while the units of mass and length remain unaltered \*.

The two readings may easily be distinguished from each other. Thus if we wish to assert physical identity or physical equivalence we might write

$$[\text{force}] \equiv [M] [L] [T^{-2}].$$

If we wish to lay stress on the variational reading, and to exclude the suggestion of physical identity, we might write

$$[\text{force}] [=] [M] [L] [T^{-2}].$$

We have already seen that the starting point in dimensional analysis is always the measurement of phenomena and the establishment of a quantitative law of variation. The laws of variation are converted into equations by the introduction of constants. The question whether such a constant is dimensional or undimensional may arise. This question is equivalent to asking : Does the determination of its magnitude depend upon the assignment of a unit of its own kind ? A constant of this kind can by transposition be brought to one side of the equation by itself. If this constant then is not expressed in terms of a unit of its own kind, it is clear that all the units or changeables on the other side must cancel out, and the dimensions disappear.

Let us take Joule's Law as an example. We may state this law briefly thus :

Work expended  $\propto$  heat generated, or

$$w = jh.$$

The constant  $j$  involved in this law refers to a physical equivalence between heat and work, which in the present state of science is believed to remain exactly the same whatever the medium in which, and the kinds of matter between which, the action takes place, and whatever the surrounding circumstances. But it is not measured in a unit of its own kind. It is simply a correlating factor introduced in order to express the known physical equivalence between  $w$  and  $h$  by

\* B. A. Report on Electrical Standards, 1863, Appendix C.

means of an equation. Consequently if we write

$$\frac{w}{h} = j$$

the physically variable quantities entering into  $w$  and  $h$  which are so related dimensionally as to make the equation  $w=hj$  homogeneous must cancel out, leaving  $j$  without dimensions.

The considerations urged by Sir A. W. Rücker, in his paper on "Suppressed Dimensions" \* show, however, that factors which have been introduced in this way ought in some cases to be regarded as having dimensions. If it is desired to distinguish such dimensional quantities from undimensional quantities, it becomes apparent that a criterion is furnished by the question : *Does the law hold without qualification of any sort ; or, in other words, is the quantity absolutely constant, independently of changes in the circumstances, in the media, or in the kinds of matter between which the action takes place ?*

## II. Dimensions of Mass, Length, and Time.

In the conventional system of dimensions the units of mass, length, and time are regarded as independent fundamental units. At the same time it has been recognized that other selections might be made, and certain other selections have been discussed \*. It has also been pointed out that mass could apparently be resolved dimensionally into length and time †, but the significance of this fact for the theory of dimensions does not appear to have been generally realized. It is proposed to discuss in this and succeeding sections some of the consequences of this further dimensional analysis.

1. The laws of variation embodied in the conventional system comprise certain geometrical and kinetic principles, which looked at as physical laws are axiomatic and not the result of special experimental inquiry. In addition to these the second law of motion is made use of. The possibility of further dimensional analysis depends upon the introduction of another law, viz. : the law of gravitation. This law holds

\* Phil. Mag. vol. xxvii. p. 104.

† Ency. Britt. Art. 'Dimensions,' Maxwell ; 'Treatise on Electricity and Magnetism,' Maxwell, vol. i. p. 3.

without qualification, irrespectively of differences in the kinds of matter considered, or of the medium through which the action takes place, and therefore possesses the characteristics requisite for the establishment of dimensional relations. The constant introduced into the variational formula below may be taken to be undimensional, since it does not represent a variable property capable of being measured by a unit of its own kind.

The dimensions of mass may be thus deduced: Consider the gravitational action of a body A of mass  $m$ , or a body B of mass  $m^1$  at a distance  $l$ . Then if  $f$  denotes the resulting acceleration of the body B, so that  $m^1 f$  denotes the force acting on it, the law of gravitation is compendiously expressed by the variational formula

$$\frac{mm^1}{l^2} \propto m^1 f.$$

This is converted into an equation by the Newtonian constant of gravitation  $G$ , thus:

$$\frac{mm^1}{l^2} G = m^1 f.$$

From this follows the dimensional relation

$$[M] = [L^3] [T^{-2}].$$

Maxwell \* deduces this same result from the formula for the space passed over in a given time by a body subject to a uniform acceleration, by substituting for the acceleration the value  $\frac{m}{l^2}$ . The law of the periodic time of a simple pendulum may be recognized if the relation be written

$$T^2 = \frac{L^3}{M} = \frac{L}{\bar{M}}.$$

The same relation is embodied in Kepler's Third Law; and in accordance therewith the astronomical unit of mass might be defined, in terms of length and time, to be a mass such that a small satellite moving round it in an orbit of unit radius would have unit angular velocity.

\* 'Treatise on Electricity and Magnetism,' vol. i. p. 3.



In the discussion on Mr. Williams' paper on 'Dimensions'\*, it was pointed out by Mr. Madan that when the astronomical unit of mass is employed it could be regarded as having the dimensions  $[L^3] [T^{-2}]$ . To this it was objected by Professor Boys that Mr. Madan was arguing in a circle, since the equation  $[M] [L] [T^{-2}] = [M^2] [L^{-2}]$  could not be true unless the Newtonian constant was introduced on the right-hand side. This objection disappears, I think, on examination. It is not as if the Newtonian constant were dependent for its value on the kinds of matter considered, or as if it were constant only within the limits of a given system and had different values for different systems. This constant is supposed to have the same value whatever the range of application and whatever the circumstances. In these respects it stands on altogether a different footing from the dielectric constants  $\mu$  and  $k$  to which in the discussion referred to Professor Boys compared it. The quantities  $\mu$  and  $k$ , even if constant for given media, are different for different media. And while such quantities must be regarded as having dimensions, constants of the class to which  $G$  belongs can be regarded as undimensional. They conform to the criterion for undimensional quantities set out in the preceding section.

2. It has been remarked in the preceding section that dimensional equations are sometimes regarded as expressing physical identity or physical equivalence, and sometimes as expressing merely a law of relative variation between the measures of qualitatively distinct phenomena.

The assignment of the dimensions of mass in terms of length and time requires to be examined from each of these points of view. We may first examine the result on the supposition that the dimensional equation merely expresses a relation of quantitative variation. We should then, as previously suggested, write the equation

$$[M] [=] [L^3] [T^{-2}]$$

and this would be understood to mean, the unit of mass is defined to vary in magnitude directly as the cube of the change ratio of the unit of length, and inversely as the square of the change ratio of the unit of time. The correlation

\* 'Nature,' vol. xlvii. p. 116; Phil. Mag. vol. xxxiv. (1892) p. 234.

between units is thus carried a step further than in the conventional system, and the independent units are thereby reduced to two. There would, moreover, be no difficulty, on this interpretation of the dimensional relation, in carrying the correlation of units still another step, by introducing the further convention or definition that the magnitude of the units of length and time should, if varied, always be maintained in direct proportion one to the other. This convention would be denoted by the formula

$$[T] [=] [L].$$

Observations on this latter aspect of the matter may, however, be deferred until the dimensional analysis of mass has been examined in the light of the opposed view as to the significance of dimensional formulæ.

In respect to this view, we can not, I think, avoid regarding mass as an ultimate and unanalysable datum. As Mr. Williams says in his paper on 'Dimensions'\*, it stands for tangibility in general, which we can in no way think as built up from time and space elements. How, then, are we to regard this dimensional relation between mass, length, and time? We seem to be required to look upon mass as complex.

But we can not conceive mass as a complex capable of being analysed into constituents. We are compelled to accept it as an ultimate fact; an irresolvable datum beyond which we can not go. How, then, can the requirement of homogeneity be satisfied?

Let  $F$  be any fundamental quantity in terms of which  $x, y, z$  may be expressed.

Let it be assumed that

$$x = F^a$$

$$y = F^b$$

$$z = F^c;$$

then, if

$$z^r = \frac{x^p}{y^q},$$

it follows that

$$F^{cr} = \frac{F^{ap}}{F^{bq}};$$

\* Phil. Mag. vol. xxxiv. (1892) p. 259.

and in order that this may be homogeneous

$$ap = bq + cr.$$

In the particular case before us,  $p=3$ ,  $q=2$ ,  $r=1$ ; hence the condition becomes

$$3a = 2b + c.$$

If any of the quantities  $x$ ,  $y$ ,  $z$  be itself chosen as the fundamental, this condition can be satisfied in an indefinite number of ways by the indices of the other two. If, in particular,  $x$  be the quantity selected as fundamental, so that  $a=1$ , it is necessary that  $2b+c=3$ . If fractional indices are to be avoided, it follows that  $b=c=a=1$ .

The dimensional relation

$$[M] = [L^3] [T^{-2}],$$

combined with the supposition that mass is a fundamental or simple quantity of one degree, therefore necessitates the further relations

$$[M] = [L] = [T].$$

This result is not consistent with the supposition in the light of which we are examining the dimensional analysis of mass. It is clear that the reading  $[M] \equiv [T] = [L]$  is excluded. Although the reading of the dimensional equation as an identity or physical equivalence may very well apply to complexes of ultimates, we find that this reading becomes inapplicable to equations in which one ultimate is correlated with others. We are forced to conclude that there is no way of making the equation homogeneous except on the supposition that the equation merely represents a relation of quantitative variation, and should be read

$$[M] [=] [L^3] [T^{-2}].$$

This becomes homogeneous if we make the convention that the dimensional relation  $[L] [=] [T]$  shall hold. The meaning of this is that the magnitudes of the units of length and time are, if varied, to be made to vary in direct proportion one to the other, with the result that then the unit of mass will also as a consequence vary in the same ratio. The reason for making an arbitrary convention of this character is, that it is shown by the preceding discussion to

be the last and necessary step to the correlation of all dynamical units. That it is permissible physically will be shown in the next section.

### III. *Theoretical Completion of the Correlation of the Units of Dynamical Quantities.*

It has been seen that the purpose of dimensional analysis is to render the equations embodying physical relations homogeneous with regard to some independent changeable or variable; and that the means whereby this is effected is the adoption of conventions or definitions whereby the units of qualitatively different phenomena are correlated one with another, both dimensionally and in magnitude. In the common system, however, this correlation of units stops when mass, length, and time are reached; these three are left independent of each other. In the preceding sections of this paper it has been shown that dimensional analysis and correlation of units can be carried further; and that all dynamical units can be correlated with any one only of the three fundamental quantities. This correlation would appear to require for its theoretical completion some indication of the nature of a single physical standard to which all dynamical units might conceivably be referred.

A few remarks on this point seem called for.

In the first place, it must not be thought that the present observations are intended as a suggestion that a new system of units should be adopted. The object is merely to justify in principle the introduction of the dimensional relation,

$$[L] [=] [T],$$

by pointing out that this correlation admits of being conceived to be embodied in a single standard.

Such standard is evidently some movement; and the physical law,—and every dimensional relation must embody some physical law,—is in this case the first law of motion. Any actual movement which is permanently the same would serve as the ultimate standard, if definite portions of the movement could be identified. Mean Time is already determined in this way, viz., by reference to the diurnal rotation of the earth. It is conceivable, then, that the move-

ment of some point on the earth's surface might be taken as the ultimate standard of reference for all dynamical units. A portion of this movement, if some definite portion could be identified, would give simultaneously a unit of time and a unit of length, the magnitudes of which would be proportioned one to the other. Maxwell's suggestion \*, that sodium light might be made to furnish a universal standard of length, also affords an application similar in principle to the above. The velocity of propagation of such light through the æther being constant, a unit of length and time are simultaneously obtained in principle by selecting a definite portion of the wave. In the case of the earth, the cyclical character of the apparent movement of the heavens, and in the case of the ætheric disturbance the existence of phases and phase-differences in the wave, render the identification of portions of the movements in each case conceivable.

The units of length and time being fixed, that of mass at once follows from Kepler's Law, in the manner previously pointed out. Having thus obtained theoretically the units of mass, length, and time in proper correlation each to the others, all the units dealt with in the conventional system are thereby correlated in like manner.

#### IV. *One outcome of Dimensional Analysis may be the Suppression of all Qualitative Distinctions.*

The first point that stands out clearly in the interpretation of the result reached in the preceding sections is, that when we have pushed dimensional analysis as far as it will go in the direction we have been pursuing it, we have abandoned all the distinctive characters of the phenomena with which we start, except that they have quantity.

This is apparent from the consideration that any dimensional formula will have exactly the same form, whether written in terms of L or M or T. Not only is this the case, but quantities like momentum, work, quantity of heat, and (saving the presence of  $k$  and  $\mu$ ) electric and magnetic charges also all reduce to unit-power of one of these. It therefore follows that any one of them could be substituted indifferently for any one of the fundamental units.

\* 'Treatise on Electricity and Magnetism,' vol. i. p. 3.

The view that dimensional analysis may in certain cases involve the suppression of qualitative distinctions, explains the result under examination. It would lead us to the conclusion that dimensional analysis might be pushed until qualitative distinctions had become suppressed entirely. The result under discussion shows that this point has been reached when all the quantities treated have by complete correlation of units been expressed in terms of a single independent variable or changeable.

We may denote the undifferentiated quantity or unit at which we thus arrive by  $[Q]$ . The final stage of dimensional analysis of those physical phenomena possessing simple quantity is then represented thus :

$$[H] [=] [W] [=] [M] [=] [L] [=] [T] [=] [Q].$$

Other units, it will be found by substitution, are expressed by different powers of  $[Q]$ , some positive and some negative, but all integral. This is merely indicative of the fact that the measures of other phenomena are mathematically related to those referred to as possessing simple quantity by integration or differentiation.

The fact that the attempt to correlate completely all the units of dynamical quantities leads ultimately to the suppression of all physical distinctions, affords a logical ground for a practice which otherwise seems to be difficult to justify in principle. It is usual to consider the physical interpretation of mathematical equations only at the beginning and end of a mathematical investigation, on account of the possible appearance of uninterpretable terms in the course of mathematical analysis \*. If, however, the conclusions set out above be sound, so soon as physical relations have been reduced to mathematical expression, it is optional to us to regard the units as completely correlated in principle, and the phenomena as having therefore been robbed implicitly of every attribute but pure quantity. And consequently there is no need to consider the mathematical procedure in the course of analysis in any other light than that of purely quantitative relation.

\* Maxwell, *Encyc. Britt.*, Art. Dimensions.

### V. *Fundamental, Derived, and Secondary Units.*

The application of the considerations set out above to electric, magnetic, and thermal units, shows that the usual manner of conceiving the distinctions between fundamental, derived, and secondary units may require revision. The distinction ought not to rest on whether the phenomenon is ultimate or not. The true distinction would appear to be between those quantities the units of which can be completely correlated with other units, and thereby be made dependent on them, and those which cannot be correlated with other units, and therefore remain independent. At the same time the distinction between dependent and independent units should be regarded as analogous to that between chemical elements and chemical compounds.

The want of a quantitative law connecting variations of the dielectric constants with differences in the media through which electric and magnetic actions are transmitted, has been shown by Sir A. W. Rücker in his paper on suppressed dimensions\* to necessitate the introduction of independent units for the measurement of these two quantities. Similar considerations apply to thermal units. Specific heat, for instance, is sometimes made undimensional by a process that would make every physical quantity undimensional†. The mass of a body, to take this as an example, is always the ratio of one mass to another, the mass of the body to unit mass; or  $\frac{M}{M}$ , which according to this treatment would have no dimensions. We may be unable to specify any law of sufficient generality to establish the dimensions of specific heat, and therefore it may not be possible to say more than that the specific heat of water is unit specific heat. But if this be done, we have another independent unit which ought to appear in the dimensional formulæ of thermal quantities. Thus from the relation

$$sm\theta = h$$

we should obtain the dimensions of temperature,

$$[\theta] = [L^2] [T^{-2}] [s^{-1}],$$

\* Phil. Mag. vol. xxvii. p. 104.

† 'Textbook of Physics,' Watson, p. 339.

and of entropy,

$$[\Phi] = [M] [s].$$

The list of independent units should apparently then be reduced in some directions and enlarged in others. One independent unit at least seems to be required for each of the principal divisions of physics not yet brought wholly within the sphere of dynamics. Given this, the units in each department can be correlated with one another and with those in other departments. The independent quantity in thermodynamics may be specific heat, that of electricity, specific inductive capacity, that of magnetism, permeability, and that of chemistry perhaps atomic weight, or chemical equivalent.

#### VI. *Systems of Dimensions and Remarks on Annexed Tables.*

The annexed tables comprise a selection of material illustrating various points discussed in the preceding sections. Column 3 in Table A shows the conventional system of dimensions of certain mechanical quantities, and the corresponding column in Table C shows those of certain electrical and magnetic quantities in electromagnetic measure. On the left of each of these is placed the result of eliminating M by substituting therefor the value  $L^3T^{-2}$ , and on the left again, in column 1, is placed the result of eliminating all qualitative distinction by the substitution of Q for each of the fundamental units. Similar columns are shown in Table B, derived in the same way from the third column, the origination of which will be described later.

While on the one side, by correlation of the units employed, the conventional dimensions admit of being simplified down to the Q column, on the other side we are free to introduce additional qualitative distinctions beyond those which are embodied in the conventional system. There may indeed be considerable latitude of choice in the construction of systems of dimensions, owing to there being no one law of variation, or group of laws, connecting phenomena, which on theoretical grounds is entitled to recognition to the exclusion of all others. In illustration of this, a few examples are given in the annexed tables of the way in which dimensional systems may be worked out when based on different fundamental laws



from those on which the conventional system is based. In the conventional system of dimensions of mechanical quantities, a certain selection of which is given in column 3 of Table A, the measurement of force and of work are based on the second law of motion. The fourth column gives different dimensions for some of these quantities obtained by referring the measurement of force to the law of gravitation. In whatever way the units of mass, length, and time are fixed, it is conceivable that the unit of force might be fixed with reference to the gravitational stress between two unit masses at unit distance apart. The column under consideration shows the dimensions which on this basis must be assigned to force, work, and elasticity. Column 5 in Table C shows the dimensions of certain electric and magnetic quantities referred to Faraday's laws of electrodeposition. In these,  $z$  is the electrochemical equivalent of the deposited metal, and  $m$  the mass of metal deposited by a current  $C$  in a time  $t$ . The dimensions of electric quantity  $q$  are obtained at once from the law

$$m = zCt = zq ;$$

the remaining dimensions are obtained from the same relations among electric and magnetic quantities as those made use of in the conventional system. It will be seen that  $z$  in this system occupies a position similar to that of  $k$  and  $\mu$  in Sir A. W. Rücker's systems.

In Table B, column 4, is given a series of dimensions for thermal quantities embodying specific heat as a fundamental quantity, in accordance with the suggestion in the preceding section. By reference to Faraday's Laws of Electrolysis and Dulong and Petit's Law of Atomic Heat, a hypothetical system of dimensions of thermal quantities independent of specific heat may, however, be arrived at. According to the law of atomic heats, the thermal capacities of the atoms of different substances in the solid state are all equal. Hence the number of atoms  $N_a$  in a given mass will be proportional to the thermal capacity of the mass ; or

$$N_a \propto \frac{h}{\theta},$$

where  $h$  is the quantity of heat necessary to raise the temperature of the mass an amount  $\theta$ . According to Faraday's

TABLE A.—Systems of Dimensions of Mechanical Quantities.

	In terms of [Q]. (1)	Elimination of M. (2)	Conventional System. (3)	Gravitational System. (4)
Fundamental Units.	Q	L; T.	L; M; T.	L; M; T.
Mass .....	$Q^1$	$L^3T^{-2}$	M	M
Velocity .....	$Q^0$	$L T^{-1}$	$LT^{-1}$	$LT^{-1}$
Momentum .....	$Q^1$	$L^4T^{-3}$	$MLT^{-1}$	$MLT^{-1}$
Force .....	$Q^0$	$L^4T^{-4}$	$MLT^{-2}$	$M^2L^{-2}$
Work .....	$Q^1$	$L^5T^{-4}$	$ML^2T^{-2}$	$M^2L^{-1}$
Elasticity .....	$Q^{-2}$	$L^2T^{-4}$	$ML^{-1}T^{-2}$	$M^2L^{-4}$

TABLE B.—Systems of Dimensions of Thermal Quantities.

	In terms of [Q]. (1)	Elimination of M. (2)	Hypothetical System based on Thermo- and Electro- chemical Relations. (3)	Introduction of Specific Heat, $s$ . (4)
Fundamental Units.	Q	L; T.	L; M; T.	L; M; T; $s$ .
Quantity of Heat ..	$Q^1$	$L^6T^{-4}$	$ML^2T^{-2}$	$ML^2T^{-2}$
Temperature .....	$Q^0$	$L^3T^{-3}$	$M^{\frac{1}{2}}L^{\frac{1}{2}}T^{-2}$	$L^2T^{-2}s^{-1}$
Entropy .....	$Q^1$	$L^2T^{-1}$	$M^{\frac{1}{2}}L^{\frac{1}{2}}$	$M_s$
Specific Thermal Conductivity. }	$Q^0$	$LT^{-1}$	$M^{\frac{1}{2}}L^{-\frac{1}{2}}T^{-1}$	$ML^{-1}T^{-1}s$
Specific Entropic Conductivity. }	$Q^{-1}$	$L^{-2}T$	$L^{-2}T$	$ML^{-3}Ts^2$

TABLE C.—Systems of Dimensions of Electrical and Magnetic Quantities.

Fundamental Units.	in terms of [Q].	Elimination of M from Conventional Electro-magnetic System.	Conventional Electro-magnetic System.	Conventional Electrostatic System with Electro-magnetic Work as in column (4) Table A.	Electro-chemical System.	Prof. J. J. Thomson's Modification of Sir A. W. Rucker's Systems.		Mr. Williams' System (Electromagnetic) based on distinction of Directions.
						Electrostatic. (5)	Electromagnetic. (7)	
	(1)	(2)	(3)	(4)	(5)			(8)
	Q	L; T.	L; M; T.	L; M; T.	L; M; T; $\epsilon$ .	L; M; T; $k$ ; $p$ .	L; M; T; $\mu$ ; $p$ .	R; M; T; X; Y; Z; $\mu$ .
Electric Quantity,.....	Q <sup>1</sup>	L <sup>2</sup> T <sup>-1</sup>	M <sup>1</sup> L <sup>1</sup>	M	$\epsilon^{-1}$ M	$k^{\frac{1}{2}}M^{\frac{1}{2}}L^{\frac{1}{2}}T^{-1}$	$p\mu^{-\frac{1}{2}}M^{\frac{1}{2}}L^{\frac{1}{2}}$	$\mu^{-\frac{1}{2}}M^{\frac{1}{2}}RX^{-\frac{1}{2}}Y^{\frac{1}{2}}Z^{-\frac{1}{2}}$
Current .....	Q <sup>0</sup>	L <sup>2</sup> T <sup>-2</sup>	M <sup>1</sup> L <sup>1</sup> T <sup>-1</sup>	MT <sup>-1</sup>	$\epsilon^{-1}MT^{-1}$	$k^{\frac{1}{2}}M^{\frac{1}{2}}L^{\frac{1}{2}}T^{-2}$	$p\mu^{-\frac{1}{2}}M^{\frac{1}{2}}L^{\frac{1}{2}}T^{-1}$	$\mu^{-\frac{1}{2}}M^{\frac{1}{2}}RT^{-1}X^{-\frac{1}{2}}Y^{\frac{1}{2}}Z^{\frac{1}{2}}$
Potential; E.M.F. ...	Q <sup>0</sup>	L <sup>2</sup> T <sup>-3</sup>	M <sup>1</sup> L <sup>1</sup> T <sup>-2</sup>	ML <sup>-1</sup>	$\epsilon L^2T^{-2}$	$k^{-\frac{1}{2}}M^{\frac{1}{2}}L^{\frac{1}{2}}T^{-1}$	$p^{-1}\mu^{\frac{1}{2}}M^{\frac{1}{2}}L^{\frac{1}{2}}T^{-2}$	$\mu^{\frac{1}{2}}M^{\frac{1}{2}}RT^{-2}X^{\frac{1}{2}}Y^{-\frac{1}{2}}Z^{\frac{1}{2}}$
Resistance .....	Q <sup>0</sup>	LT <sup>-1</sup>	LT <sup>-1</sup>	L <sup>-1</sup> T	$\epsilon^2M^{-1}L^2T^{-1}$	$k^{-1}L^{-1}T$	$p^{-2}\mu LT^{-1}$	$\mu T^{-1}X$
Intensity of Electric Field .....	Q <sup>-1</sup>	L <sup>2</sup> T <sup>-3</sup>	M <sup>1</sup> L <sup>1</sup> T <sup>-2</sup>	ML <sup>-2</sup>	$\epsilon LT^{-2}$	$k^{-\frac{1}{2}}M^{\frac{1}{2}}L^{-\frac{1}{2}}T^{-1}$	$p^{-1}\mu^{\frac{1}{2}}M^{\frac{1}{2}}L^{\frac{1}{2}}T^{-2}$	$\mu^{\frac{1}{2}}M^{\frac{1}{2}}R^{-1}T^{-1}Y^{-2}X^{\frac{1}{2}}Y^{-\frac{1}{2}}Z^{\frac{1}{2}}$
Magnetic Quantity ...	Q <sup>1</sup>	L <sup>2</sup> T <sup>-2</sup>	M <sup>1</sup> L <sup>1</sup> T <sup>-1</sup>	ML <sup>-1</sup> T	$\epsilon L^2T^{-1}$	$p k^{-\frac{1}{2}}M^{\frac{1}{2}}L^{\frac{1}{2}}$	$\mu^{\frac{1}{2}}M^{\frac{1}{2}}L^{\frac{1}{2}}T^{-1}$	$\mu^{\frac{1}{2}}M^{\frac{1}{2}}RT^{-1}X^{\frac{1}{2}}Y^{-\frac{1}{2}}Z^{\frac{1}{2}}$
Magnetic Flux ..... (Intensity $\times$ Area)	Q <sup>1</sup>	L <sup>2</sup> T <sup>-2</sup>	M <sup>1</sup> L <sup>1</sup> T <sup>-1</sup>	MLT <sup>-1</sup>	$\epsilon^{-1}MLT^{-1}$	$p^{-1}k^{\frac{1}{2}}M^{\frac{1}{2}}L^{\frac{1}{2}}T^{-2}$	$\mu^{-\frac{1}{2}}M^{\frac{1}{2}}L^{\frac{1}{2}}T^{-1}$	$\mu^{-\frac{1}{2}}M^{\frac{1}{2}}RT^{-1}X^{\frac{1}{2}}Y^{-\frac{1}{2}}Z^{\frac{1}{2}}$
Magnetic Potential ...	Q <sup>0</sup>	L <sup>2</sup> T <sup>-2</sup>	M <sup>1</sup> L <sup>1</sup> T <sup>-1</sup>	MT <sup>-1</sup>	$\epsilon^{-1}MT^{-1}$	$p^{-1}k^{\frac{1}{2}}M^{\frac{1}{2}}L^{\frac{1}{2}}T^{-2}$	$\mu^{-\frac{1}{2}}M^{\frac{1}{2}}L^{\frac{1}{2}}T^{-1}$	$\mu^{-\frac{1}{2}}M^{\frac{1}{2}}RT^{-1}X^{-\frac{1}{2}}Y^{\frac{1}{2}}Z^{-\frac{1}{2}}$
Reluctance.....	Q <sup>-1</sup>	L <sup>-1</sup>	L <sup>-1</sup>	L <sup>-1</sup>	L <sup>-1</sup>	L <sup>-1</sup>	L <sup>-1</sup>	X <sup>-1</sup> YZ <sup>-1</sup>
Intensity of Mag- netic Field.....	Q <sup>-1</sup>	L <sup>2</sup> T <sup>-2</sup>	M <sup>1</sup> L <sup>1</sup> T <sup>-1</sup>	ML <sup>-1</sup> T <sup>-1</sup>	$\epsilon^{-1}ML^{-1}T^{-1}$	$p^{-1}k^{\frac{1}{2}}M^{\frac{1}{2}}L^{\frac{1}{2}}T^{-2}$	$\mu^{-\frac{1}{2}}M^{\frac{1}{2}}L^{-\frac{1}{2}}T^{-1}$	$\mu^{-\frac{1}{2}}M^{\frac{1}{2}}RT^{-1}(XYZ)^{-\frac{1}{2}}$

Laws the quantities of electricity carried by chemical equivalents of the different deposited ions are all equal. Hence the number of equivalents  $N_e$  in a given electrolytically deposited mass will be proportional to the total quantity  $q$  of electricity carried during the deposition; or

$$N_e \propto q.$$

Hence in each series of substances in which, for the same mass,  $N_a$  is equal to or bears a constant ratio to  $N_e$ , that is in each series having the same chemical valency, we have

$$\frac{h}{\theta} \propto N_a \propto N_e \propto q.$$

Whence

$$\theta \propto \frac{h}{q},$$

Putting in the dimensions for  $h$  and  $q$ , we find suggested for the dimensions of  $\theta$  the following:—

$$[\theta] = \frac{ML^2T^{-2}}{M^{\frac{1}{2}}L^{\frac{1}{2}}} = M^{\frac{1}{2}}L^{\frac{3}{2}}T^{-2}.$$

Now, as we have already seen in connexion with the dimensions of atomic weight, Dulong and Petit's Law of atomic heats does not in its existing form possess all the characters necessary to the establishment of dimensional relations. It does not follow, however, that if it could be modified so as to become an exact law containing all the conditions on which its truth depends, the dimensional relations would necessarily be altered. In fact, if the correction took the form merely of added terms, the dimensional relations would remain the same. In view of these considerations, and the agreement of the indices in column 3 and 4 to be referred to presently, and of the analogies which these dimensions lead to, it may be worth while to adopt them tentatively.

It is interesting to observe, in the first place, that the dimensions of temperature on this basis become the same as those of electromotive force. This reminds us that temperature may be regarded as thermomotive force, that property at each point of a heated body which determines the direction and rapidity of the flow of heat: Entropy also assumes the dimensions of electric quantity; and while specific thermal

conductivity still retains some complexity, yet if we divide by temperature so as to obtain the dimensions of specific conductivity for entropy, we arrive at the same dimensions as those of specific electric conductivity.

Since in Table A we have three different series of dimensions for mechanical quantities, and such quantities enter at several points into electrical and magnetic quantities, of which we have three dimensional systems in Table C, viz. the electrostatic, the electromagnetic, and the electrochemical, we may by combination obtain nine systems of dimensions for electrical and magnetic quantities. One of these is given, by way of example, in column 4, Table C, which gives the conventional electrostatic system with force and work measured by reference to the law of gravitation. It may be noticed that both in this column and in column 2 the indices of the fundamental units are all integral. This is only what might be expected, when we consider that in both we have introduced an inverse square law in connexion with mechanical force as well as in connexion with the electric and magnetic forces. The fractional indices in the dimensions of electric and magnetic quantities arise from the electric and magnetic forces being measured with reference to an inverse square law, while measures of mechanical force are referred to the simple proportion embodied in the second law of motion. In view of this, it is by no means clear that the introduction of the dimensions of the dielectric constants would necessarily convert all these indices into whole numbers.

The remaining columns in Table C comprise the dimensions of the selected quantities in electrostatic and electromagnetic measure according to the systems set out in Prof. J. J. Thomson's 'Treatise on Electricity and Magnetism,' and those of the same quantities in electromagnetic measure in Mr. Williams' system. Now the dimensions in columns 5 to 8 only in Table C are complete; those in columns 1 to 4 are simplified by the conventional suppressions. In every case, however, the reduction to the Q column, both in Table B and in Table C, is unaffected by the omission of  $s$ ,  $z$ ,  $k$ ,  $\mu$ ,  $p$ . In other words, in spite of the diversity in these systems as to the portion of each dimensional formula thrown into these factors, the sum of the indices of L, M, and T in the remaining

portion is for each formula the same. This suggests that the dimensions of the conventionally suppressed quantities must satisfy the condition that the sum of the indices in each shall be zero, and also affords a ready check on the accuracy of any dimensional formula when another formula is known or is deducible.

There is one remark to be made in conclusion as to the principle involved in Mr. Williams' system of dimensions, viz. the preservation in the dimensional formula of a distinction between lengths measured parallel to the three Cartesian axes of coordinates. The remark is that this principle would admit of extension to masses and times as well as to lengths. In the ordinary dimensional formula, mass is denoted by  $M$ , and is regarded only as having inertia. But we have seen that a mass might enter into a dimensional formula not merely as inertia, but as a gravitating or as an electro-deposited mass, or in other ways. Such masses might be distinguished in the dimensional formulæ by means of a subscript letter. Times might be distinguished again according to whether they represent continuous flux or periodic times. To illustrate this point, let us determine the dimensions of electric resistance, distinguishing between gravitating matter ( $M_g$ ), mass or inertia ( $M_i$ ), and electro-deposited matter ( $M_e$ ), and introducing Mr. Williams' distinctions of direction. Electro-chemically the dimensions of current are  $z^{-1}(M_e)T^{-1}$ , the dimensions of electromotive force are  $\left[ \frac{\text{work}}{\text{electric quantity}} \right]$ , and those of resistance are  $\left[ \frac{E}{C} \right]$ . Hence, if we measure work by reference to the law of gravitation, as in Table A column 4, and electric quantity electrostatically, we obtain the following dimensions for electric resistance :—

$$k^{-\frac{1}{2}}z(M_g)^2(M_e)^{-1}(M_i)^{-\frac{1}{2}}R^{-1}(XYZ)^{-\frac{1}{2}}T^2.$$

Such formulæ would represent in some measure the joint bearing of the different laws connecting the physical properties of the body on each property considered separately. This treatment exemplifies what has been called a movement up the scale of qualitative distinction in a direction diametrically opposite to that pursued in the conventional dimensional analysis.

In conclusion, I desire to acknowledge that I have had the advantage of discussing with my friend Mr. Sowter the subjects of this paper, in the preparation of which he has taken great interest.

# XLI. *Note on Dimensions of Physical Quantities.*

By R. J. SOWTER, *B.Sc., A.R.C.Sc.\**

MR. RAVENSHEAR in his paper on dimensional analysis of physical quantities has shown that any physical quantity,  $Q$  say, is expressible in terms of the dynamical quantities,  $L$ ,  $M$ , and  $T$ , in different ways, but that all the various ways are related to or connected with one another by an index law. Thus :—

$$Q = \mu^a (L^a M^b T^c) = \kappa^b (L^{a'} M^{b'} T^{c'}) = \gamma^c (L^{a''} M^{b''} T^{c''}) = q^d (D^n),$$

and

$$\alpha + \beta + \gamma = \alpha' + \beta' + \gamma' = \alpha'' + \beta'' + \gamma'' = n.$$

Now this index law not only affords a useful working check in dimensional analysis, but in my opinion it appears to be pregnant with suggestion, and calls for careful consideration. It is obvious that one interpretation is that the dynamical factors are complete in themselves; that is,  $\mu^a$ ,  $\kappa^b$ ,  $\gamma^c$ ,  $q^d$  do not contain dynamical factors, or are not rationalizing factors in a dynamical sense, and that these factors show the various ways in which quantitative measurements of the physical quantity  $Q$  are made. The dynamical factors consequently express change-ratios, and have no qualitative significance. The things  $Q$  and  $(L^a M^b T^c)$  are then related in their quantitative measurements merely, they are not identifiable qualitatively. This view seems to me to be logically complete in itself, and is probably the aspect of dimensional analysis conceived by Fourier.

The other interpretation, namely, that  $(L^a M^b T^c) \dots (D^n)$  are stamped with qualitative significance requires the factors  $\mu$ ,  $\kappa$ , &c. to be dynamically related, and does not require that any index law should hold. It is immaterial with this view whether  $(\alpha + \beta + \gamma)$  is or is not equal to  $(\alpha' + \beta' + \gamma')$ , the only

\* Read April 24, 1903.

condition necessary is that

$$\frac{\mu^a}{\kappa^b} = \frac{L^a M^b T^c}{L^a M^b T^c}.$$

Now this view requires all physical quantities to be expressible completely in dynamical terms, that is, Laplace's doctrine of a dynamical universe must be accepted. Advances are being made in this direction; but the logical position of this complete dynamical resolution of the physical universe, it must be admitted, is not more forward than in the time of Laplace. This interpretation is by no means logically complete.

That view which relates all things capable of quantitative measurement through quantity alone seems to be thrust upon us by the facts, although the whole endeavour and trend of modern physics is to explain things dynamically. The factors  $\mu^a$ ,  $\kappa^b$ , &c., that we have been compelled to introduce into the various branches of physics carry with them the physical qualities or characteristics of the quantities associated with them.

The elimination of physical significance from any dynamical factor in the expression for a physical quantity does not appear to lead to failure along any line of argument. Further, elimination of physical significance can be applied to dynamical quantities themselves; so that, accepting this hypothesis, physical quantities, including dynamical quantities, can all be conceived to have a measuring dynamical factor. For example, (Velocity)  $v = A \left( \frac{L}{T} \right)$  would be looked on as measured by  $L/T$ , but to have the quality of  $A$ . That is,  $A$  is here a velocity.

Also, if we consider Electric quantity  $Q$ ,

$$Q = z^{-1} M = \kappa^{\frac{1}{2}} (M^{\frac{1}{2}} L^{\frac{1}{2}} T^{-1}) = \mu^{-\frac{1}{2}} (M^{\frac{1}{2}} L^{\frac{1}{2}}),$$

and rob the dynamical factors of physical significance, then

$$(Q) = (z^{-1}) = (\kappa^{\frac{1}{2}}) = (\mu^{-\frac{1}{2}}),$$

that is,  $Q$  is physically like  $\frac{1}{z}$ ,  $\sqrt{\kappa}$ , and  $\frac{1}{\sqrt{\mu}}$ ; and  $\frac{1}{z}$ ,  $\sqrt{\kappa}$ ,  $\frac{1}{\sqrt{\mu}}$  are all physically alike or qualitatively similar. These



factors must, on this hypothesis, be conceived as associated, say as æther factors.

Any physical quantity, on this hypothesis, is expressible as

$$Q = N(D^n)g,$$

where  $N$  is a mere number,  $(D^n)$  is a dynamical factor indicating a quantitative measurement process, and  $g$  is a quality factor of the nature of  $Q$ .

#### DISCUSSION ON THE TWO FOREGOING PAPERS.

Prof. EVERETT said that the possibility of making two fundamental units suffice instead of three, by taking advantage of the law of gravitational attraction, was nothing new, but was expounded and worked out in some of its applications in ordinary text-books. The proposal to diminish the number of fundamental units by making the unit of length proportional to the unit time, simply amounted to the adoption of a fundamental unit of velocity to take the place of a unit length, and was no simplification. The supposed new law of indices appeared to be simply the well-known principle by which information as to physical relations could often be deduced from consideration of dimensions: by which, for example, it could be shown that the velocity of sound must vary directly as the square root of elasticity and inversely as the square root of density.

Mr. PRICE referred to the fact that the author had determined the dimensions of mass in terms of length and time from the equation  $f = m^2/l^2$ , considering  $G$ , the Newtonian constant of gravitation, as a quantity without dimensions. He thought that if all suppressed dimensions were properly introduced and proper attention paid to the direction of vector quantities, then the dimensions of a quantity gave an idea of its nature, and quantities having the same dimensions were identical in their natures.

Prof. S. P. THOMPSON said he had read the paper through, and thought it brought the subject no further forward. There were several statements which were so surprising that it was necessary to give them consideration. For instance, we were asked to believe that a scalar, like mass, was of the same dimensions and nature as a vector, like length, and that

both of these were physically the same as time. There is no distinction at all in the paper between scalars and vectors. The author's criterion for an undimensional quantity was a false one, and led to obviously incorrect results. Taking the formula  $F=Ma$ , he (Prof. Thompson) said that, using the author's criterion, mass had no dimensions. The criterion also made  $G$ , the Newtonian constant, an undimensional quantity. Referring to the equation  $Q=N(D^n)g$  given in Mr. Sowter's Note, he thought that the right-hand side might contain a fourth letter representing a geometrical operator. Mr. Ravenshear in his paper had retained fractional exponents which were meaningless and could not possibly exist.

Mr. RAVENSHEAR said that much of the criticism appeared to him to be based upon misunderstandings of his position and the propositions he had advanced. He did not think that  $G$  necessarily had no dimensions. His contention was that, owing to its universal constancy, to give it dimensions was not logically compulsory, and therefore it was optional to work out the consequences of both alternatives. He would have preferred that Prof. Thompson had criticized his criterion using Joule's equivalent, the example dealt with in his paper. The example used by Prof. Thompson did not satisfy the criterion, since masses might have any magnitude. He had not advocated the retention of irrational indices, but had put in a plea for two or three systems in which all the indices were integral. Prof. Everett had discussed the matter as though a new system of units was being proposed for practical adoption. Mr. Ravenshear said that, on the contrary, his object was merely the logical analysis of the principles underlying the use of units. He had not proposed to use velocity in place of length or time, but contended that a permanent motion furnished in a single standard two units from which all other dynamical units could in principle be derived.

Mr. SOWTER said that Mr. Ravenshear had shown an alternative method of rationalizing irrational expressions. Referring to Prof. Thompson's observation that the equation  $Q=N(D^n)g$  required a further term representing a geometrical operator, he pointed out that if different directions

are accounted for by symbols, these take their places in the dynamical or measuring factors ( $D^a$ ), so that any physical quantity need only be expressed by the three factors set forth. As regards Prof. Everett's remark on the index law, he was aware of the application of dimensional analysis to the solution of certain physical problems, but he was not aware that the index law had been formulated and the deductions based upon it dealt with previously.

**XLII. *On the Comparison of Vapour-Temperatures at Equal Pressures.* By Professor J. D. EVERETT, F.R.S.**

RAMSAY and YOUNG seem to have been the first to call attention (Phil. Mag. Jan. 1886) to the fact that the ratio  $t/t'$  of the absolute temperatures at which two vapours (at saturation) have the same pressure  $p$  remains nearly constant for changes of  $p$  of very considerable magnitude. In the case of vapours of kindred constitution, their results show that a twentyfold increase of  $p$  only changes  $t/t'$  by about  $\frac{1}{2}$  per cent.

They further lay down, for the comparison of vapours generally, the law—now known as “Ramsay and Young's law”—that if  $t_1, t_2$  denote the absolute temperatures of one vapour at the pressures  $p_1, p_2$ , and  $t'_1, t'_2$  those of another vapour at the same pressures, we shall have

$$\frac{t_2}{t'_2} - \frac{t_1}{t'_1} = c(t_2 - t_1), \quad . . . . . (1)$$

$c$  being a small positive or negative constant multiplier, depending on the substances compared.

To the eye of the mathematician there is an awkward one-sidedness about this formula; it is not symmetrical as between  $t$  and  $t'$ . It can, however, be rendered symmetrical by first writing it in the form

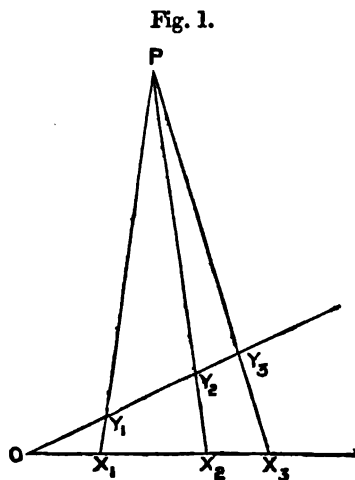
$$\frac{t}{t'} - ct = k,$$

( $k$  being a constant), and then dividing by  $ct$ . We thus obtain an equation of the form

$$\frac{x}{t} + \frac{y}{t'} = 1, \quad . . . . . (2)$$

$x$  and  $y$  standing for  $-k/c$  and  $1/c$ , which are constants. A straight line making intercepts  $t, t'$  on the axes is represented by equation (2) and will pass through the fixed point  $x = -k/c, y = 1/c$ . In practice  $k$  is positive; hence one of the two coordinates of the fixed point is positive and the other negative. As  $c$  is small, the point is at a considerable distance.

Ramsay and Young's law is thus equivalent to the following statement (see fig. 1):—*If the absolute temperatures*



*at which two vapours have equal pressures are represented by lengths O X, O Y laid off along two lines inclined at any angle, the line X Y joining their extremities will, when produced, pass through a fixed point P lying at a considerable distance. Two pairs of corresponding temperatures (preferably far apart) are theoretically sufficient to determine the position of P; and then the temperature of one substance corresponding to a given temperature of the other is found by merely drawing a line through two given points.*

It is not necessary to use the same scale for  $t'$  as for  $t$ ; for equation (2) may be written

$$\frac{x}{t} + \frac{2y}{2t'} = 1,$$

showing that the effect of doubling the scale for  $t'$  is simply to double the ordinate  $y$  of the fixed point. A table given by Ramsay and Young shows that the absolute temperature of mercury vapour is rather more than double that of ether vapour at the same pressure. The scale for mercury might therefore be conveniently taken double of that for ether.

The best general formula that has been propounded for the relation between  $t$  and  $p$  is Rankine's, which is discussed in the first of his 'Collected Papers,' and shown to give good results for very various substances. His tables of steam-pressure were calculated by it. It is

$$\log p = \alpha - \frac{\beta}{t} - \frac{\gamma}{t^2}, \quad . . . . . (3)$$

the second and third terms being in practice always negative.

If we omit the third term, as Rankine does in cases where the data are not very accurate, we have, for two vapours

$$\log p = \alpha - \frac{\beta}{t} = \alpha' - \frac{\beta'}{t'}, \quad . . . . . (4)$$

whence

$$\frac{\beta}{t} - \frac{\beta'}{t'} = \alpha - \alpha',$$

indicating that the line  $XY$  passes through the fixed point

$$x = \frac{\beta}{\alpha - \alpha'}, \quad y = -\frac{\beta'}{\alpha - \alpha'}.$$

Ramsay and Young's law is thus deducible from Rankine's shortened formula.

Treating Rankine's full formula in the same way, we get

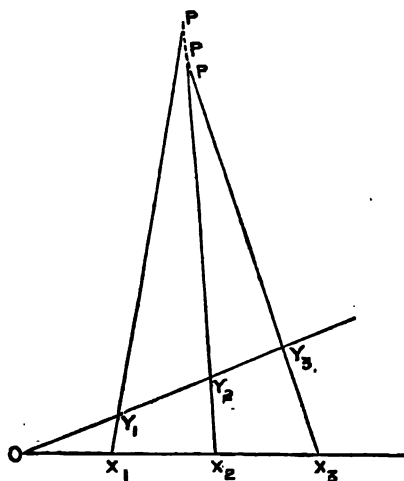
$$\frac{\beta + \gamma/t}{t} - \frac{\beta' + \gamma'/t'}{t'} = \alpha - \alpha',$$

showing that the ultimate intersection of two consecutive positions of  $XY$  is

$$x = \frac{\beta + \gamma/t}{\alpha - \alpha'}, \quad y = -\frac{\beta' + \gamma'/t'}{\alpha - \alpha'} \quad \dots (5)$$

As  $t$  and  $t'$  increase, the absolute magnitudes of  $x$  and  $y$  diminish. Instead of strictly meeting in a point  $P$ , as in fig. 1, the lines  $XY$  will accordingly touch a curve with its concavity turned away from the origin, like the dotted curve  $PP P$  in fig. 2.

Fig..2.



The fact that Ramsay and Young's formula is deducible from Rankine's shortened formula is indicated by Ayrton and Perry in a paper to the Physical Society\*, in which the accuracy of Rankine's complete formula is strongly insisted on.

11 Leopold Road, Ealing, W.

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\* Phil. Mag. [5] xxi. p. 255; Proc. Phys. Soc. vii. p. 372 (1886).

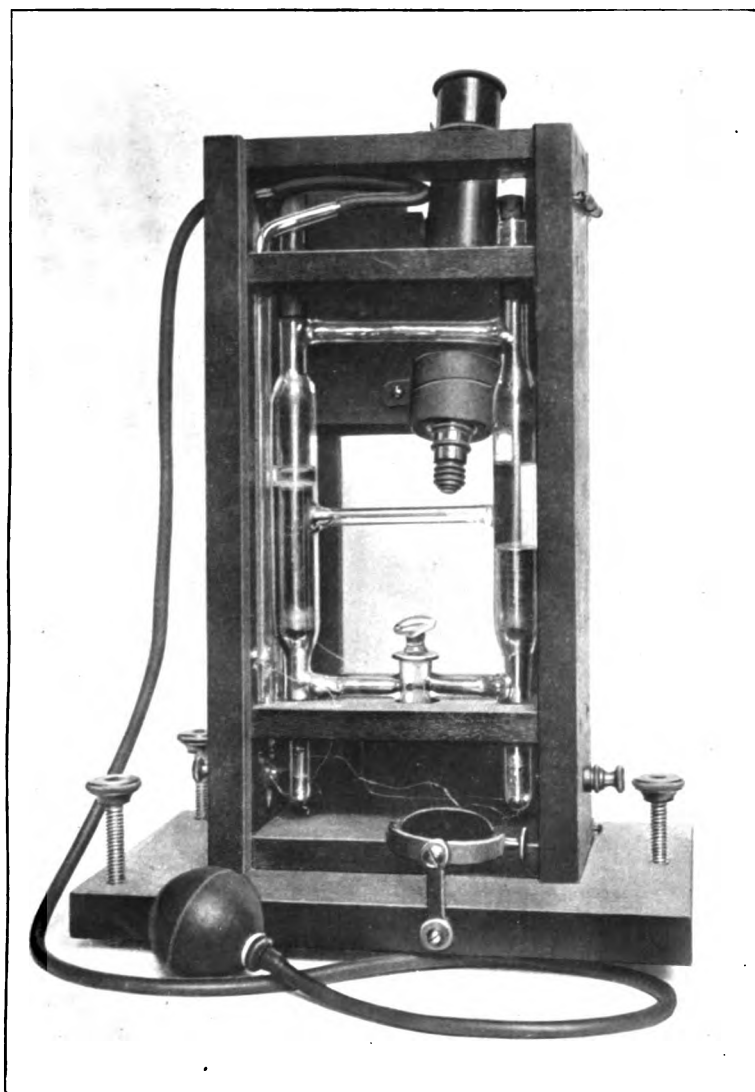






Fig. 1.

A I B



XLIII. *On the Theory of the Quadrant Electrometer.* By  
GEORGE W. WALKER, M.A., A.R.C.Sc., Fellow of Trinity  
College, Cambridge\*.

FOR the purpose of some experiments which I am taking up, I have found it necessary to examine the theory of a symmetrical quadrant electrometer more carefully than I have formerly had occasion to do. The results seem to me to be of considerable importance.

The late Dr. John Hopkinson† pointed out the imperfection of the usual formula given in Maxwell‡, and also gave an empirical formula which closely represented his experiments. The general result is well known, namely, that the sensibility of the electrometer rises to a maximum as the potential of the needle is raised, and that any further increase in the potential of the needle reduces the sensibility.

The same effect occurs in the extremely sensitive electrometers made by Bartels, of Göttingen, several of which have been in use in the Cavendish Laboratory for some time. In these instruments the needle is made of silvered paper, and hung by a single quartz fibre. The quadrants are about 5 cms. radius by 1 cm. deep, and the air-space between the quadrants is about 1 mm. The quadrants are mounted on ebonite, and are not adjustable.

There is no guard-tube for the fibre, and no leyden-jar attached, the insulation being extremely good. With the needle charged to about 100 volts, a deflexion of 1000 mms. per volt, on a scale about 1 metre from the mirror, can readily be obtained, the needle being nearly dead-beat at this sensibility, and quite steady. The shift of the needle during charging is generally but a small fraction of the deflexion for 1 volt. A maximum sensibility occurs at about 100 volts, but this of course depends on the fineness of the fibre. The sensibility seems to go on diminishing after this, at least until very high voltages are used.

\* Read January 23, 1903.

† Phil. Mag. [5] vol. xix. 1885, p. 291.

‡ 'Electricity and Magnetism,' vol. i.

In examining the theory I found that Hopkinson's formula could be readily explained.

The referee to whom my paper was sent pointed out that my conclusions conflicted with the experiments of Ayrton and Sumpner \* on a White pattern electrometer. I have therefore added to my paper a discussion of their results.

It will be convenient to give my modified theory of a symmetrical instrument first, and then compare my conclusions with Ayrton and Sumpner's results.

Let us first indicate the usual theory. Suppose  $V_1$ ,  $V_2$ , and  $V_3$  are the potentials of the two pairs of quadrants and the needle respectively.

The energy of the system is given by

$$E = \frac{1}{2}c_{11}V_1^2 + \frac{1}{2}c_{22}V_2^2 + \frac{1}{2}c_{33}V_3^2 + c_{12}V_1V_2 + c_{13}V_1V_3 + c_{23}V_2V_3, \quad (1)$$

and the force in the direction  $\theta$  is given by

$$\frac{1}{2} \frac{\partial c_{11}}{\partial \theta} V_1^2 + \frac{1}{2} \frac{\partial c_{22}}{\partial \theta} V_2^2 + \frac{1}{2} \frac{\partial c_{33}}{\partial \theta} V_3^2 + \frac{\partial c_{12}}{\partial \theta} V_1V_2 + \frac{\partial c_{13}}{\partial \theta} V_1V_3 + \frac{\partial c_{23}}{\partial \theta} V_2V_3. \quad (2)$$

It is next proved, somewhat doubtfully, that

$$\frac{\partial c_{11}}{\partial \theta} = -\frac{\partial c_{22}}{\partial \theta} = -\frac{\partial c_{13}}{\partial \theta} = +\frac{\partial c_{23}}{\partial \theta}$$

$$\frac{\partial c_{12}}{\partial \theta} = \frac{\partial c_{33}}{\partial \theta} = 0,$$

and hence, if the couple due to the fibre is  $F\theta$ , we get

$$F\theta = \frac{\partial c_{23}}{\partial \theta} (V_2 - V_1) \{V_3 - \frac{1}{2}(V_1 + V_2)\}. \quad (3)$$

In the above process no exception can be taken to (1) and (2); but in the remaining part of the proof the values of the differential coefficients are calculated for  $\theta = 0$ .

This is not valid. Formula (2) is only true provided the quantities are reckoned for the displaced position.

In what follows I shall assume perfect symmetry of the arrangements.

Let  $c_{11} = a_0 + \sum_1^\infty a_n \theta^n$ ,

where  $a_0$  etc. are constants independent of  $\theta$ .

\* Phil. Trans. 1891, vol. clxxxii. p. 519.

Then by symmetry we obtain

$$c_{22} = a_0 + \sum_1^{\infty} (-)^n a_n \theta^n.$$

Again, let

$$c_{13} = b_0 + \sum_1^{\infty} b_n \theta^n,$$

the condition of symmetry gives us

$$c_{33} = b_0 + \sum_1^{\infty} (-)^n b_n \theta^n.$$

Further, it is clear that  $c_{12}$  and  $c_{33}$  must be even functions of  $\theta$ . Hence let us take

$$c_{12} = c_0 + \sum_1^{\infty} c_{2m} \theta^{2m}$$

$$c_{33} = d_0 + \sum_1^{\infty} d_{2m} \theta^{2m}.$$

It is clear, since the zero of potential is arbitrary, that an equal increase in each of the potentials must leave the force unchanged.

We thus get from formula (2)

$$\left. \begin{aligned} \frac{\partial c_{11}}{\partial \theta} + \frac{\partial c_{12}}{\partial \theta} + \frac{\partial c_{13}}{\partial \theta} &= 0 \\ \frac{\partial c_{22}}{\partial \theta} + \frac{\partial c_{23}}{\partial \theta} + \frac{\partial c_{13}}{\partial \theta} &= 0 \\ \frac{\partial c_{33}}{\partial \theta} + \frac{\partial c_{12}}{\partial \theta} + \frac{\partial c_{23}}{\partial \theta} &= 0 \end{aligned} \right\} \cdot \cdot \cdot \cdot \cdot \quad (4)$$

Hence, if we substitute the assumed forms for the coefficients in the system (4), we obtain

$$\sum_1^{\infty} n(a_n + b_n) \theta^{n-1} + \sum_1^{\infty} 2m c_{2m} \theta^{2m-1} = 0, \quad \cdot \cdot \cdot \cdot \quad (5)$$

$$\sum_1^{\infty} (-)^n n(a_n + b_n) \theta^{n-1} + \sum_1^{\infty} 2m c_m \theta^{2m-1} = 0, \quad \cdot \cdot \quad (6)$$

$$\sum 2m d_{2m} \theta^{2m-1} + \sum_1^{\infty} n b_n \theta^{n-1} + \sum_1^{\infty} (-)^n n b_n \theta^{n-1} = 0. \quad \cdot \quad (7)$$

We may therefore equate the coefficients of the various powers of  $\theta$  to zero.

Equations (5) and (6) lead to the same results, namely,

$$\text{For } n \text{ odd} \quad a_n + b_n = 0.$$

$$\text{For } n \text{ even} = 2m \quad a_{2m} + b_{2m} + c_{2m} = 0.$$

While equation (7) gives

$$\text{For } n \text{ even} = 2m \quad d_{2m} + 2b_{2m} = 0.$$

Hence we get for the coefficients of capacity

$$\begin{aligned}c_{11} &= a_0 + \sum_1^{\infty} a_n \theta^n, \\c_{22} &= a_0 + \sum_1^{\infty} (-)^n a_n \theta^n, \\c_{13} &= b_0 - \sum_1^{\infty} a_{2n-1} \theta^{2n-1} + \sum_1^{\infty} b_{2n} \theta^{2n}, \\c_{23} &= b_0 + \sum_1^{\infty} a_{2n-1} \theta^{2n-1} + \sum_1^{\infty} b_{2n} \theta^{2n}, \\c_{12} &= c_0 - \sum_1^{\infty} (a_{2n} + b_{2n}) \theta^{2n}, \\c_{33} &= d_0 - 2 \sum_1^{\infty} b_{2n} \theta^{2n}.\end{aligned}$$

We are now in a position to calculate the values of the differential coefficients, and since for the present purpose we are concerned with small displacements only, we shall proceed to first powers of  $\theta$ . We thus get

$$\begin{aligned}\frac{\partial c_{11}}{\partial \theta} &= a_1 + 2a_2 \theta, & \frac{\partial c_{12}}{\partial \theta} &= -a_1 + 2b_2 \theta, & \frac{\partial c_{13}}{\partial \theta} &= -2(a_2 + b_2) \theta, \\ \frac{\partial c_{22}}{\partial \theta} &= -a_1 + 2a_2 \theta, & \frac{\partial c_{23}}{\partial \theta} &= +a_1 + 2b_2 \theta, & \frac{\partial c_{33}}{\partial \theta} &= -4b_2 \theta.\end{aligned}$$

Substituting in (2) we obtain for the force on the needle

$$a_1(V_2 - V_1) \{V_2 - \frac{1}{2}(V_1 + V_2)\} + \theta \{a_2(V_2 - V_1)^2 - 2b_2(V_2 - V_1)(V_2 - V_2)\}$$

Hence, instead of the ordinary equation

$$F\theta = a_1(V_2 - V_1) \{V_2 - \frac{1}{2}(V_1 + V_2)\},$$

we obtain

$$\begin{aligned}\{F + 2b_2(V_2 - V_1)(V_2 - V_2) - a_2(V_2 - V_1)^2\} \theta \\ = a_1(V_2 - V_1) \{V_2 - \frac{1}{2}(V_1 + V_2)\}.\end{aligned}$$

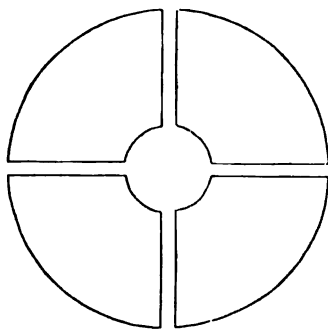
In the ordinary method of working  $V_1$  is actually zero, and  $V_2$  only slightly greater than zero, while  $V_3$  is comparatively high. We thus have approximately the formula

$$\{F + 2b_2V_3^2\} \theta = a_1(V_2 - V_1)V_3. \quad . \quad . \quad (8)$$

This equation exactly represents the results in Bartel's electrometer, and shows that if  $b_2$  is positive there will be a maximum sensibility depending on the potential of the needle. The higher the attempted sensibility, by reducing  $F$  and increasing  $V_3$ , the more important does the term  $b_2V_3^2$  become.

Can we then account for a positive value of  $b_2$ ?

Let us consider how  $c_{23}$  varies with the displacement. If there were no air-gap between the quadrants, it is clear that  $c_{23}$  would remain constant in all positions of the needle, but in practice the air-gap is not negligible. For example, suppose the quadrants are 5 cms. radius, and the air-gap 1 mm. wide, then the ratio of the air-gap to the area of the quadrants is about 2 sq. cms. to 75 sq. cms.



The capacity of the needle  $c_{23}$  will thus vary, depending on the number of lines of force which escape the quadrants.

We clearly have stationary values at  $\theta=0$  and  $\theta=\frac{\pi}{4}$  or

$$\frac{\partial c_{23}}{\partial \theta} = 0 \text{ for } \theta=0 \text{ and } \theta=\frac{\pi}{4}.$$

First suppose the angle of the needle  $90^\circ$ . Then as we move from the position  $\theta=0$  both edges of the needle approach an air-space, and therefore  $c_{23}$  diminishes. It will continue to diminish to  $\theta=\frac{\pi}{4}$ , where it is least. The curve will therefore be as shown in fig. (1), and the quantity  $b_2$  is positive.

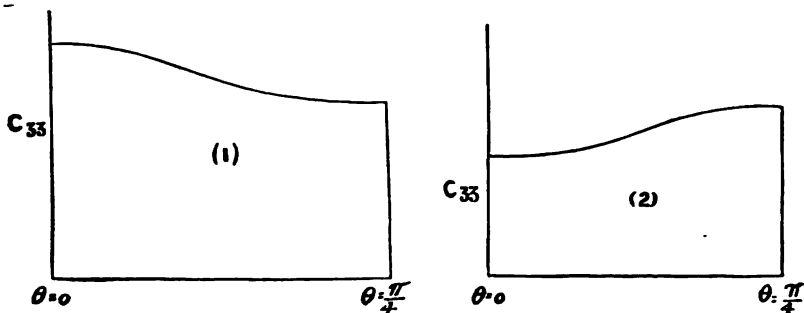
Second, suppose the needle to be a mere wire, then  $c_{23}$  continually increases from  $\theta=0$  to  $\theta=\frac{\pi}{4}$ , and the curve is as shown in fig. (2) (p. 458).

In this case  $b_2$  is negative. For angles of the needle near  $90^\circ$  we may therefore suppose that  $b_2$  is +, while it is probable that there is an angle between  $0^\circ$  and  $90^\circ$  for which  $b_2$  might be made actually zero.

Further it is clear that  $b_2$  must diminish as the air-gap is reduced, and hence the potential for maximum sensibility increased, other things being equal.

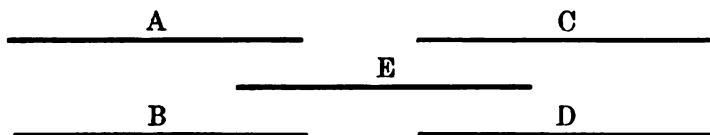
So far the argument is qualitative, and we have now to get a quantitative estimate of the effect of the air-gap.

Let us take the case of a quartz fibre 5 cms. long, .009 mm. diameter. For this  $F = 8 \times 10^{-3}$ . Now if  $2b_2 = 10^{-22}$ , and  $V_2 = 100$  volts, we get  $2b_2 V_2^2 = 10^{-3}$ . This is a quantity of the same order as  $F$ . Hence if  $2b_2$  is only  $\frac{1}{10}$  of an electrostatic unit of capacity, there would in this case be a maximum sensibility at about 100 volts.



The solution of the electrical distribution for a system like the quadrant electrometer is a well-nigh hopeless problem. I now propose to discuss a two-dimensional problem, which in some respects corresponds to the actual case considered in the preceding pages. I have succeeded in solving the problem completely, and the result confirms my view that the air-gap is sufficient to account for a maximum sensibility.

We shall take four semi-infinite plates to correspond to the upper and lower plates of the quadrants, and a plate of finite breadth to correspond to the needle.

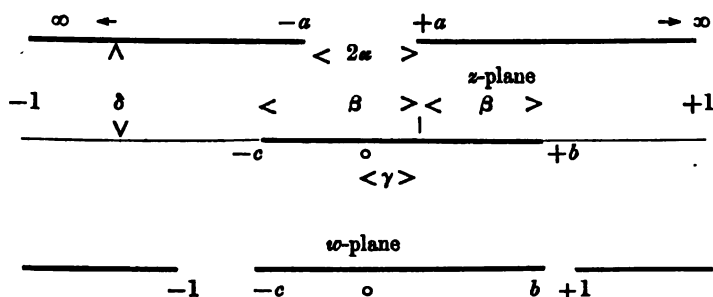


The cross-section of the arrangement is shown in the diagram : and it is to be understood that the plates A and B extend indefinitely to the left, while C and D extend indefinitely to the right. The plate E is situated midway between the two pairs of plates, and displaced from the symmetrical position.

This problem is soluble by the Schwarzian method, so that



I think it would be superfluous to give the details of the solution. I shall therefore indicate the transformations, and give the final solution :—



The plane of the needle is a plane of symmetry, and we may transform the given problem in the  $z$ -plane into the problem indicated in the  $w$ -plane, the points of correspondence being marked as I have shown.

The transformation is

$$z = -\frac{2\delta}{\pi} \left\{ \frac{w}{a^2-1} - \frac{1}{2} \log \frac{w+1}{w-1} - i\frac{\pi}{2} \right\}.$$

Let  $2a$  be the breadth of the air-gap,

$2\beta$  „ „ „ needle,

$\gamma$  „ displacement from the zero position,

$2\delta$  „ distance between the upper and lower pair of plates.

Then we have the following equations to determine  $a$ ,  $b$ , and  $c$  :—

$$\frac{a}{a^2-1} - \frac{1}{2} \log \frac{a+1}{a-1} = \frac{\pi}{2} \cdot \frac{a}{\delta} \quad . . . . (9)$$

$$\frac{1}{2} \log \frac{1+b}{1-b} - \frac{b}{a^2-1} = \frac{\pi}{2} \cdot \frac{\beta+\gamma}{\delta} \quad . . . (10)$$

$$\frac{1}{2} \log \frac{1+c}{1-c} - \frac{c}{a^2-1} = \frac{\pi}{2} \cdot \frac{\beta-\gamma}{\delta} \quad . . . (11)$$

We may note that these give a real value for  $a$  greater than unity, and real values for  $b$  and  $c$  less than unity when  $\gamma$  is  $< \beta$ . When  $\gamma$  is zero, the values of  $b$  and  $c$  are equal.

The solution of the  $w$ -problem can be effected by the transformation

$$\frac{\partial\phi + i\psi}{\partial w} = \frac{iB}{\sqrt{(w^2-1)(w-b)(w+c)}},$$

where  $\phi$  and  $\psi$  are the potential and stream-function respectively.

The latter transformation is reducible by means of elliptic functions. When we write the condition that the finite plate is at unit potential, while the semi-infinite plates are at zero potential, we readily find that the charge on the finite plate is  $\frac{4K'}{K}$ , where  $K'$  and  $K$  are the usual quarter periods of the elliptic functions, and the modulus is given by

$$k^2 = \left\{ \frac{\lambda' - b\lambda}{\lambda - b\lambda'} \right\}^2$$

$$\text{and} \quad (\lambda^2 + \lambda'^2)(b-c) - 2\lambda\lambda'(1-bc) = 0.$$

Let us put

$$b = b_0 + \delta_0$$

$$c = b_0 - \delta_0$$

and take the root

$$\frac{\lambda}{\lambda_1} = \frac{1 - b_0^2 + \delta_0^2 + \sqrt{(1 - b_0^2 + \delta_0^2)^2 - 4\delta_0^2}}{2\delta_0} = \frac{\xi}{2\delta_0} \text{ say,}$$

$$\text{we get} \quad k'^2 = b_0^2 \left\{ \frac{\xi}{\xi - 2\delta_0^2} \right\}^2.$$

If  $\delta_0$  be small we get

$$k'^2 = b_0^2 \left\{ 1 + \frac{2\delta_0^2}{1 - b_0^2} \right\}.$$

Let  $b_0'$  be the root of

$$\frac{1}{2} \log \frac{1 + b_0'}{1 - b_0'} - \frac{b_0'}{a^2 - 1} = \frac{\pi}{2} \cdot \frac{\beta}{\delta}.$$

Then we find from equations (10) and (11)

$$b_0 = b_0' \left\{ 1 - \frac{a^2 - 1}{(a^2 + b_0'^2 - 2)(1 - b_0'^2)} \delta_0^2 \right\}$$

and

$$\delta_0 = \frac{\pi\gamma}{2\delta} \frac{(1 - b_0'^2)(a^2 - 1)}{(a^2 + b_0'^2 - 2)},$$

and hence

$$k'^2 = b_0'^2 \left\{ 1 - \frac{1}{2} \frac{\pi^2 \gamma^2 (1 - b_0'^2)(a^2 - 1)^2}{\delta^2 (a^2 + b_0'^2 - 2)^3} \right\}.$$

The variation in  $k^2$  will thus be negative or positive according as  $a^2-1 >$  or  $< 1-b_0'^2$ . The formula would be invalid if  $(a^2-1)=(1-b_0'^2)$ . A brief examination shows that with a finite breadth of needle  $a^2-1$  is  $>1-b_0'^2$ .

Consider the function

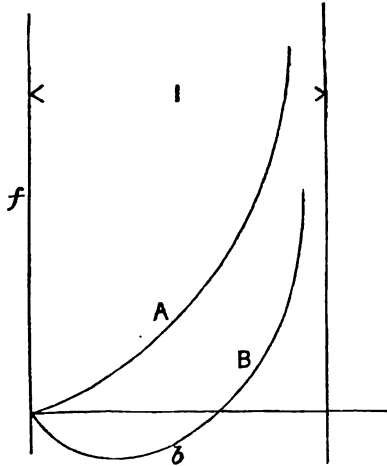
$$f = \frac{1}{2} \log \frac{1+b}{1-b} - \frac{b}{a^2-1}.$$

Then  $f=0$  when  $b=0$ ,

and  $f=+\infty$  when  $b=1$ ,

$$\frac{\partial f}{\partial b} = \frac{a^2-1+b^2-1}{(1-b^2)(a^2-1)}.$$

Now  $\frac{\partial f}{\partial b}$  will vanish when  $a^2-1=1-b^2$  or  $b^2=2-a^2$ . Hence, if  $a^2$  is  $<2$ , there is a real value for which  $\frac{\partial f}{\partial b}$  vanishes; but if  $a^2$  is  $>2$ , there is no real value. There are thus two cases, A and B, as shown in the figure.



Now the root  $b_0'$  is given by the intersection of the curve

$$f = \frac{1}{2} \log \frac{1+b}{1-b} - \frac{b}{a^2-1}$$

with the straight line

$$f = \frac{\pi}{2} \frac{\beta}{\delta}.$$

Hence, at the intersection  $\frac{\partial f}{\partial b}$  must be positive, that is,  $a^2 - 1$  is  $> 1 - b_0'^2$ .

We have seen that the capacity of the plate per unit of length perpendicular to the plane of the paper is

$$\frac{4K'}{K},$$

and  $K'$  is the same function of  $k'^2$  that  $K$  is of  $k^2$ .

Now let  $\Delta k'^2$  be the variation of  $k'^2$  from its value in the symmetrical position, then

$$\Delta k^2 + \Delta k'^2 = 0.$$

Hence the capacity

$$= \frac{4K_0'}{K_0} \left\{ 1 + \left( \frac{1}{K'} \frac{\partial K'}{\partial k'^2} + \frac{1}{K} \frac{\partial K}{\partial k^2} \right)_0 \Delta k'^2 \right\}.$$

By a curious formula in elliptic functions we have

$$\frac{1}{K'} \frac{\partial K'}{\partial k'^2} + \frac{1}{K} \frac{\partial K}{\partial k^2} = \frac{\pi}{4k^2 k'^2 K K'}.$$

Hence the capacity

$$= \frac{4K_0'}{K_0} \left\{ 1 + \frac{\pi}{4k^2 k'^2 K_0 K_0'} \Delta k'^2 \right\},$$

and we have

$$k_0'^2 = b_0'^2$$

$$k_0^2 = 1 - b_0'^2$$

and

$$\Delta k^2 = -\frac{1}{2} \frac{\pi^2 \gamma^2}{\delta^2} \frac{k_0^2 k_0'^2 (a^2 - 1)^2}{(a^2 + b_0'^2 - 2)^{\frac{3}{2}}},$$

where the suffix 0 refers to the values when  $\gamma = 0$ .

Hence the capacity is

$$= \frac{4K_0'}{K_0} \left\{ 1 - \frac{\pi^2}{8} \frac{(a^2 - 1)^2}{K_0 K_0' (a^2 + b_0'^2 - 2)^{\frac{3}{2}}} \frac{\gamma^2}{\delta^2} \right\}. \quad (12)$$

This formula corresponds to the formula which I gave in the early part of this paper for the capacity of the needle, viz.

$$c_{ss} = d_0 - 2b_2 \theta^2,$$

$\theta$  being the angular deflexion.

I showed there that if  $b_2$  was a positive quantity of order  $\frac{1}{10}$  of an electrostatic unit, the experimental peculiarity of

the electrometer for increasing potential of the needle could be accounted for both qualitatively and quantitatively.

I have therefore prepared the following numerical table, making use of Legendre's Tables for  $K$  and Hutton's Tables of Napierian Logarithms. Throughout I have taken  $\delta$  as 1 cm.

No.	$a_0$	$b_0'$	$K_0'$	$K_0$	$\alpha$ in cms.	$\beta$ in cms.	$\frac{4K_0'}{K_0}$	$\frac{\pi^2}{8} \frac{(a^2-1)^2}{K_0 K_0' (a^2+b_0'^2-2)^2}$	$\frac{\pi^2}{8} \frac{(a^2-1)^2}{K_0 K_0' (a^2+b_0'^2-2)^2}$
(1)	1.8	.98	3.0233	1.5866	.112	1.18	7.60	.333	2.53
(2)	1.8	.99	3.3577	1.5806	.112	1.40	8.48	.291	2.46
(3)	1.8	.999	4.5006	1.5715	.112	2.13	11.2	.213	2.38
(4)	2	.9999	5.658	1.570	.074	2.94	14.4	.143	2.06
(5)	3	.9999	5.658	1.570	.0108	3.07	14.4	.054	.777
(6)	3	.98	3.0233	1.5866	.0108	1.38	7.60	.101	.767

In (1), (2), and (3) we observe that keeping the air-gap about 2 mms. the effect diminishes as the breadth of the needle increases.

In (2) and (6), where the breadth is practically the same, we see the diminishing effect of the air-gap as the gap is diminished. At the same time the gap could not practically be reduced to  $\frac{1}{2}$  mm., and the variation, although reduced, is still important. I think that this investigation may be held to show that the air-gap as usually found in an electrometer is quite sufficient to account for the observed fact that there is a maximum sensibility depending on the potential of the needle; and the conclusion is that the ordinary formula would be more nearly obeyed with a small air-gap.

It is of interest to note what difference results when, instead of the potential, the charge of the needle is kept constant. The method already used for finding the mechanical force on the needle will still be valid provided  $V_3$  is reckoned for the displaced position.

If  ${}_0V_s$  be the potential of the needle in the zero position, we get

$$V_s = {}_0V_s - \frac{a_1}{d_0} \theta (V_s - V_1) \text{ to 1st power of } \theta.$$

Hence the force becomes

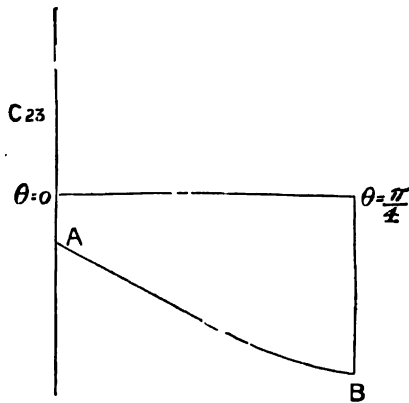
$$a_1(V_s - V_1) \left\{ {}_0V_s - \frac{1}{2}(V_1 + V_s) \right\} + \theta \left\{ \left( a_2 - \frac{a_1^2}{d_0} \right) (V_s - V_1)^2 - 2b_2(V_s - V_1)(V_s - V_2) \right\}$$

$a_1$  appears to be about  $10^{-21}$ ,

and  $d_0$  „ „ „  $10^{-19}$ .

So that as long as the potentials of the quadrants are kept small, no practical difference results.

It is important to point out that although diminishing the air-gap raises the potential of maximum sensibility, it does not follow that higher sensibility will be obtained by reducing the air-gap. This depends on  $a_1$ . The form of curve for  $c_{23}$  is shown.



Diminishing the air-gap will move the whole curve down, and B probably more than A.  $a_1$ , which is the angle made by the tangent at A, probably increases numerically as the air-gap is reduced, but whereas  $b_2$  tends to zero as the air-gap is reduced,  $a_1$  tends to a finite limit. I therefore think it probable that higher sensibility will be attained by reducing the air-gap.

We have now to consider Ayrton and Sumpner's results with the White electrometer bifilar suspension. They found a maximum about 1200 volts, but after falling a little the sensibility curve rises as the potential of the needle increases. They show most satisfactorily that the effect is due to lack of symmetry, and particularly to lack of symmetry of the guard-tube. It is not, however, clear that this effect is the same as that obtained by Hopkinson. In his experiments the maximum occurred at about 800 volts, and thereafter the sensibility went on decreasing much more rapidly than in Ayrton and Sumpner's experiments. Further, Hopkinson's instrument was much more sensitive. Again, Ayrton and Sumpner made some experiments with a single-fibre suspension, and although they obtained greater sensibilities as the potential of the needle was increased, they did not obtain a maximum.

Returning to their experiments with the bifilar suspension and the unsymmetrical guard-tube, it is almost obvious that moving the quadrants away from the guard-tube would reduce the disturbing effect.

I therefore think that their experiments apply only to an extremely unsymmetrical instrument of comparatively low sensibility, and that the maximum considered in this paper is beyond the range of their instrument.

#### DISCUSSION.

Mr. ADDENBROOKE stated that he had studied the quadrant electrometer from a practical point of view for many years. He looked upon Hopkinson's paper, read before the Physical Society in 1885, as the basis of all work upon the electrometer. Hopkinson pointed out that in a White instrument the deflexion was proportional to the potential-difference between the needle and the quadrants up to certain voltages, and ascribed the variations in sensitiveness at high voltages to want of symmetry. Mr. Addenbrooke said that there were many things which might affect the rule that the sensibility was proportional to the potential of the needle. The field is not uniform between the quadrants, the tilting of the needle may be serious, and there may be lateral displacement if the needle is not centrally suspended. In practice the

distance between the quadrants must not be too small, and the needle should have sufficient weight. He thought that the variation in sensitiveness of different electrometers similar to the one used by the author in his experiments, would be considerably different in different instruments. There was also a difficulty with contact-errors when working with very sensitive electrometers, but it was generally possible to get rid of it by balancing. He pointed out how the formula usually employed with a quadrant electrometer could be simplified by arranging so that the potential of one set of quadrants was as much above zero as that of the other set was below.

Mr. APPLEYARD said the sensitiveness and precision of modern electrometers was largely due to the fact that the sulphuric acid vessel was dispensed with. In the older instruments, where sulphuric acid was used, a film formed upon the surface. The surface tension at the contact point of the dipping wire with this film was variable, depending upon the strength and age of the acid, and unless the acid was frequently stirred it was impossible to obtain concordant results. Moreover, the dipping-wire was sometimes not rigidly attached to the middle of the needle but suspended by a hook, so that there was a certain amount of free swing before the surface tension took effect. He objected to the author's use of the word "sensibility" for sensitiveness predicated of an instrument.

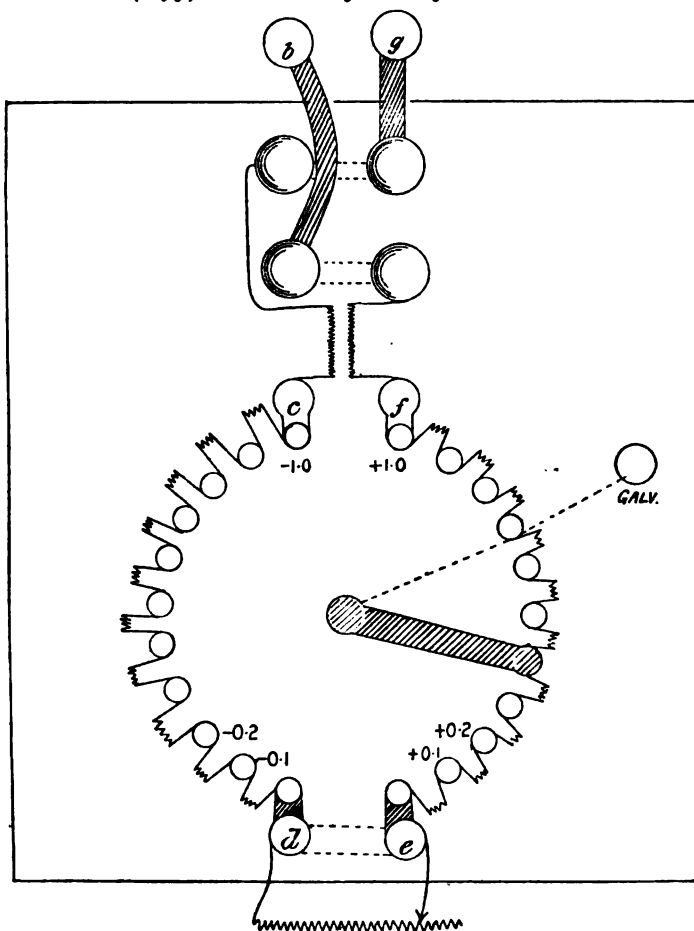
Dr. A. GRIFFITHS indicated an improved method of arriving, in an elementary manner, at the ordinary formula for the quadrant electrometer by considering the electrical energy per unit volume instead of the capacity per unit length.

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**XLIV. A Resistance Comparator.** By R. A. LEHFELDT\*.

OBJECTING to sliding contacts on account of the thermo-electric effects they tend to introduce, and irregularities slide-wires often show when a good deal used, I have designed this comparator without any. It consists of two coils of 99 ohms each (*bcfg*) connected by twenty coils of 0.1 ohm each.



The latter are arranged circularly, so that a switch connected to the galvanometer may be set on any one of the intervening

\* Read March 13, 1903.

studs. When the comparator is to be used in the ordinary way, to make a simple Wheatstone's bridge, the terminals  $d$   $e$  are connected by a short copper strap. When, as in the potentiometer-coils for the measurement of which this comparator was designed, there is an appreciable connecting resistance between the coils to be compared, the two-point bridge method is used; the strap is then removed and an adjustable resistance inserted. The ends  $b$   $g$  of the comparison resistances are connected by copper straps to the cups of a mercury commutator, and through that to a pair of large binding screws that project outside the board carrying the coils.

When the galvanometer switch is set on  $d$  or  $e$  each arm is 100 ohms; as it is moved round the dial the resistance is altered by steps of  $\frac{1}{1000}$  part. The galvanometer deflexions are taken for the two positions nearest balance and interpolation to  $\frac{1}{100}$  calculated. In this way I consider that an accuracy of one part in 100,000 is attainable.

To calibrate the comparator the two arms are adjusted to be as nearly equal as possible, and then compared by the use of a pair of nearly equal resistances measured in the usual way. Next the resistances from  $b$  to  $d$  and from  $e$  to  $g$  are separately compared with a standard 100 $\omega$ , and  $c$  to  $d$  and  $e$  to  $f$  with a standard ohm. Finally, a good box is put in parallel with  $cd$  and  $ef$  in turn and the ratio corresponding to each stud determined. This need only be done to  $\frac{1}{1000}$  part to obtain  $\frac{1}{100,000}$  in the final results.

The method of interpolating by the galvanometer has, I think, been unduly neglected. Even when one tries to carry out a strictly null experiment, one is obliged, on account of thermoelectric effects, and so on, to observe accurately minute movements of the galvanometer needle. It therefore does not introduce any new difficulty to read the galvanometer-scale exactly each time, and it may be made, as in this comparator, to avoid reading the position of a sliding contact on a scale. I think therefore that there is gain of accuracy as well as of convenience in using the interpolation method.

The galvanometric arrangements I have adopted for this purpose are as follows:—A plane mirror, 15 mm. diam., is

attached to the coil of the (D'Arsonval) galvanometer. A telescope of 25 millim. aperture is placed some 600 millim. in front, and, mounted on the telescope-tube, one of Zeiss's transparent glass scales, backed by ground-glass and illuminated by a small incandescent lamp behind. The mirror and telescope were made by Mr. Hilger: the scale is 100 millim. long, and the graduations are exceedingly fine. Altogether the definition is so good that one can read to  $\frac{1}{20}$  millim., *i. e.* to  $\frac{1}{2000}$  of the scale-length, with ease and certainty, although the scale is very short. Under these circumstances, to claim one per cent. accuracy in interpolating is well within the mark. I should like to take this opportunity of emphasizing the remark made some years ago by Professor Threlfall, that it is better to attain sensitiveness in a galvanometer by having a big mirror and first-rate optical conditions, than to push the electromagnetic sensitiveness to an extreme.

The apparatus described in this and the foregoing paper is intended for temperature measurements in an attempt at determining the Joule-Thomson effect, and was purchased out of a grant made for that purpose by the Royal Society, and I am glad to express to them my thanks for the liberality which has enabled me to undertake the work.

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#### XLV. *A Potentiometer for Thermocouple Measurements.*

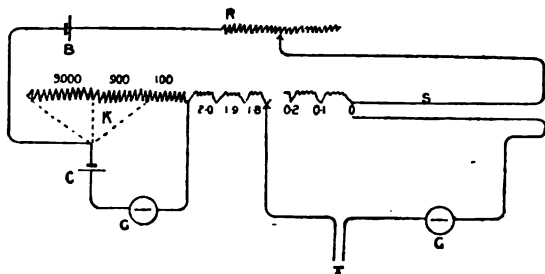
*By* R. A. LEHFELDT\*.

To make a satisfactory potentiometer for thermoelectric work, it is essential that it shall not introduce a high resistance in the circuit of the couple and galvanometer. Most of the potentiometers in the market, which answer well enough for comparing voltaic cells, fail in this respect. I have therefore devised an instrument which is shown schematically in fig. 1. From the positive terminal of the accumulator B current flows to the switch K by means of which it can be sent through 100 $\omega$  or 100 + 900 or 100 + 900 + 9000, in order to get three grades of sensitiveness: it then passes through 20

\* Read March 13, 1903.

coils of  $0.1\Omega$  each, a slide-wire of a little more than  $0.1\Omega$ , and through the adjustable resistance  $R$  back to the accumulator. The fixed resistance of 100, 1000, or 10,000 ohms is

Fig. 1.



shunted by a cadmium cell  $C$  and galvanometer  $G$ , and  $R$  adjusted till the galvanometer is balanced. The thermocouple  $T$  with galvanometer  $G$  is put across any number of the tenth-ohm coils, and any fraction of the slide-wire. Of course two galvanometers, as shown in the diagram, are not necessary: a double pole-switch puts the actual instrument into either circuit as desired.

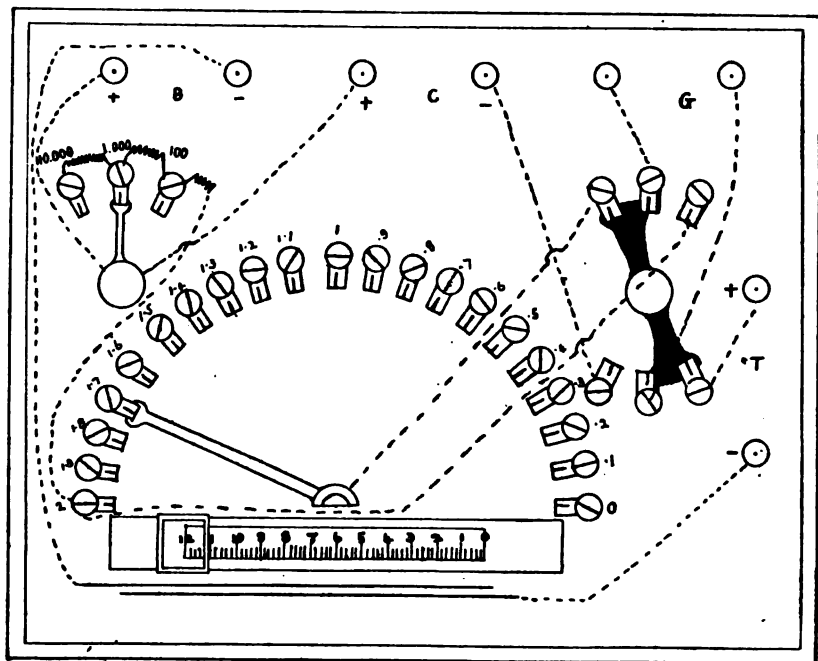
The voltage on the ends of one of the tenth-ohms (taken as unit) is then 1000- 10,000- or 100,000th part of the cadmium, *i. e.*, approximately 1000, 100, or 10 microvolts, according to the position of  $K$ .

Fig. 2 represents the actual instrument. The greatest care has been taken to avoid accidental thermoelectromotive forces, which are the chief trouble in using thermocouples. The couple I have actually used so far is constantan copper, which gives about 4000 microvolts between  $0^\circ$  and  $100^\circ$ . The only metals used in the measuring circuit are copper and manganin. All the coils are of the latter metal; the slide-wire is of gilt manganin; the galvanometer connexion is made by a short bridge between the slide-wire and a similar galvanometer wire. (These two wires are shown in the figure by the side of the scale, though actually underneath it.) The slider makes contact always, a separate key being used to put the galvanometer in circuit. The potentiometer is inclosed in a wooden case, lined with thick sheet copper and filled with paraffin-oil to keep the temperature constant, and

the two points where the copper thermocouple leads join the manganin measuring circuit are carefully buried deep down in the interior of the box and near together.

The sliding contact is carried by a block sliding on two steel bars: it is moved by a steel rod with clamping and fine adjustment screws, and its position read through a lens by means of a vernier graduated in fortieths of a millimetre.

Fig. 2.



As the wire is 100 millims. long the smallest reading is  $\frac{1}{4000}$  of the unit, which, as stated above, may be 1000, 100, or 10 microvolts; and as there are 20 tenth-ohm coils, the smallest reading is  $\frac{1}{80,000}$  of the largest.

The fineness of reading is, as a matter of fact, limited by the sensitiveness of the galvanometer used.

All the working parts are inclosed by a plate-glass lid through which only the handles project.

Outside the potentiometer itself the apparatus used consists of the accumulator (sometimes two or more); the adjustable

resistance  $R$ ; the cadmium cell; galvanometer—a highly sensitive D'Arsonval of about 20 ohms, made by the Cambridge Scientific Instrument Co.; and galvanometer key. The latter is of the usual short-circuiting reversing type, but unusually small, made of copper, and inclosed in a box from which only the ebonite studs project, for the better avoidance of thermoelectric effects.

To calibrate the instrument the procedure is as follows:—

(i.) The 100 $\omega$ , 1000 $\omega$ , and 10,000 $\omega$  resistances are compared directly with standards. To allow of this and similar operations, the heads of all the studs in the instrument carry screws. The comparison was kindly made for me at the National Physical Laboratory.

(ii.) Each tenth-ohm is compared with the succeeding one by the usual method for comparing nearly equal resistances; the slide-wire is compared with the first tenth-ohm in the same way. During these operations current is led through the coils and the voltage taken off at the same points as when the potentiometer is ordinarily in use.

(iii.) Groups of ten tenth-ohm coils in series are compared with a standard ohm by the method described in the preceding paper.

(iv.) Further, as a check on the results, two groups of ten tenth-ohm coils were measured at the National Physical Laboratory in the usual way. These measurements are of no direct use, however, as in making them current is led into and out of the coils at the points ordinarily used for taking off the voltage; hence the result differs from that obtained in (iii.) by the resistance of the studs, which is one or two ten-thousandths of an ohm.

(v.) The slide-wire is calibrated.

It would be a convenience in calibrating to provide an additional terminal, connected to the point of junction of the last tenth-ohm with the hundred-ohm coil, as this would enable one to lead in current under the usual working conditions without passing the high-resistance coil: this is desirable when calibrating the tenth-ohms, as it is safe to use pretty large currents through them. Otherwise I have found the working of the instrument satisfactory.

Before measuring a thermocouple, two tests should be

made. First, the galvanometer-key should be pressed half-way down, so that the galvanometer-circuit is broken. The needle will probably swing a little. If it swings equally on each side of its previous position of rest, there is no thermoelectric effect in the galvanometer. Second, a short piece of copper wire should be put across the thermocouple terminals and the battery-circuit broken: if then (with double-pole switch set to the thermocouple circuit) on pressing the galvanometer-key there is no deflexion, this shows absence of disturbing thermoelectric effects in the rest of the apparatus. The measurement may then be proceeded with.

XLVI. *A Direct-reading Potentiometer for Thermoelectric Work.* By J. A. HARKER, D.Sc.\*

[Plate VII.]

To anyone who has used a potentiometer for thermoelectric measurement of temperature, it will be obvious that nearly all the ordinary types of instrument have material disadvantages when employed for this purpose.

Most of the higher class potentiometers are primarily designed for direct comparison of E.M.F.'s of the order of a volt and upwards, the readings being made in most cases to about 0001 volt. With the thermojunction materials now employed for high-temperature measurement, this quantity 100 microvolts represents 6° to 10° C.; and in order to attain higher sensitivities at low ranges, special accessory apparatus is required to reduce the standard E.M.F. applied to the potentiometer to  $\frac{1}{10}$  or  $\frac{1}{100}$  of its normal value. This addition is generally accompanied by a considerable loss of proportionate sensitivity.

It is obvious that in thermoelectric work the circuit in which the E.M.F. to be measured is generated has generally a total resistance of quite a different order of magnitude to the cases most usually met with; and so far from a high resistance in the potentiometer being an advantage as in many

\* Read March 13, 1903.

cases, it is in this case detrimental to the attainment of a high sensitiveness.

The diameter and length of the wire used for thermojunctions of course varies greatly; but we shall be within the mark in saying that the total resistance of the thermojunction wire seldom exceeds 5 ohms, and that therefore a low resistance in the potentiometer is a great advantage. In the form to be described, intended for the direct measurement of E.M.F.'s up to 21,000 microvolts, the maximum resistance capable of being placed in series with the galvanometer and thermojunction is 2.1 ohms.

The instrument described represents a form which in subsequent work has proved very convenient, and which was designed and made in the National Physical Laboratory workshops, after consultation with the Director, Dr. Glazebrook, to whom I am indebted for several valuable suggestions.

Experience with several forms of Carey-Foster and Callendar-Griffiths resistance-bridges had convinced me that to calibrate to the necessary accuracy a slide-wire of such size as to make a resistance of 0.1 ohm possible with a moderate length was a difficult piece of work; and therefore several arrangements were tried with a view of rendering possible the use of a short wire of large cross-section. It is, of course, a considerably easier matter to make a thick wire much more uniform from end to end than a thin one, and the calibration to the accuracy required, especially if the wire be very short, becomes comparatively simple.

The final arrangement decided upon, after some preliminary experiments on models, I believed at first to be novel; but on searching the literature I find it has been previously used for potentiometers, and is nothing more than a low-resistance form of the Kelvin-Varley slide used in telegraphic work. A diagrammatic representation of the connexions is given in Pl. VII. fig. 1, and a plan of the top of the instrument in fig. 2. The balancing-coils on which the fall of potential is adjusted to a definite value are in two rows—the centre row of the box being twenty coils of 0.1 ohm each, and in series with these there is a second row immediately behind the slide-wire consisting of eleven coils of 0.01 ohm. By means of an arrangement of thick copper bus-bars connected with the ends of the



slide-wire, which has a total resistance of  $\cdot 02$  ohm, any two adjacent coils of this latter series may be put in parallel with the slide-wire. The eleven coils of  $\cdot 01$ , two of which are thus shunted, are equivalent to exactly  $\cdot 1$  ohm.

For all ordinary thermoelectric work the fall of potential along these two sets of coils is adjusted so that each of the back row represents 1000 microvolts, each  $\cdot 01$  being therefore 100 microvolts. The slide-wire is provided with a scale of 200 divisions figured as 100, which are practically millimetres; and as the fall along the wire is 100 microvolts,  $0\cdot 1$  microvolt can easily be estimated. It will be seen that the slide-wire thus connected acts like a vernier to the small coils.

The adjustment of the E.M.F. is made by a standard Clark or Weston cell and the auxiliary set of coils in the back row, a feature of the instrument being that without any external alteration either form of standard may be used at will. The five coils to the left are permanently connected in series, but are arranged so that any coil may be cut out of circuit when required. Their values are 100, 40, 1,  $\cdot 5$ , and  $\cdot 5$  ohms respectively. Those to the right are a set of ten simple series coils of  $\cdot 01$  ohm each arranged so that a connexion can be taken from any one of them to the long bus-bar just in front. Suppose we wish to use as a standard a Clark cell whose E.M.F. at the prevailing temperature is  $1\cdot 4333$  volts. It is obvious that we may make the E.M.F. over the  $\cdot 1$  ohm balancing-coils have the desired value of 1000 microvolts by putting into circuit the coils 100, 40, 1,  $\cdot 5$ , and 3 of the  $\cdot 01$  series, leading from the third hundredth to no. 17 of the balancing set, when altogether we shall have—

$$\begin{array}{rcl}
 100 & & \\
 40 & & \\
 1 & \left. \vphantom{\begin{array}{l} 100 \\ 40 \\ 1 \end{array}} \right\} & \text{in back row.} \\
 \cdot 5 & & \\
 \cdot 03 & & \\
 1\cdot 7 & \left. \vphantom{\begin{array}{l} 100 \\ 40 \\ 1 \end{array}} \right\} & \text{in balancing-coils and bridge-wire.} \\
 \cdot 1 & & 
 \end{array}$$

With this connexion the maximum E.M.F. measurable is 18,000 microvolts.

Should a Weston cell of E.M.F.  $1\cdot 0186$  be substituted for

the Clark, the only alteration necessary would be to short-circuit coils 40, 1, and  $\cdot 5$ , and to move the connector from the third to the sixth of the set of hundredths.

The compensating current is furnished by a small 30-ampere-hour secondary cell in series with which is a dial resistance capable of variation from  $\cdot 01$  up to 200 ohms by steps of  $\cdot 01$ .

The four thermojunction circuits provided are connected to a selector-switch, by means of which they or the difference of any two of them may be successively brought into circuit, and the change over from the standard cell-connexion required in the preliminary adjustment is made at the two-way switch at the front left-hand corner, which puts in the galvanometer to the circuit required.

Throughout the whole apparatus the only metals present carrying current are high-conductivity copper and manganin, and all connexions on the top of the box are made by means of mercury-cups. There are doubtless objections to the use of mercury in any apparatus intended to be permanent ; but as it was essential that in this instrument the contact-resistance of certain portions should be very low and constant, it was thought to be, on the whole, preferable to use well-fitting amalgamated contacts throughout, rather than any form of rubbing contact or plug.

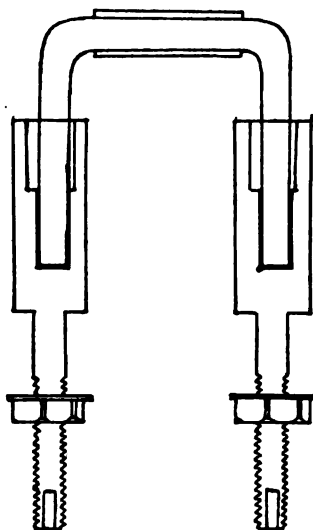
The interconnexions are made by means of a system of copper bus-bars and a form of copper mercury-cup, designed so as to be made without undue waste of material on an automatic lathe.

A pair of these cups with a connector for short-circuiting them are shown in full size in the diagram. It will be seen that the excess of mercury squeezed out of the lower hole may remain in the widened portion without overflowing.

The slide-wire, which is of manganin, is protected from oxidation by gilding, as in some of the Crompton-Fisher potentiometers. Its ends are hard-soldered to massive copper blocks, which are screwed to the transverse ends of the two bus-bars above and below the row of  $\cdot 01$  ohm balancing-coils.

In order to make the bridge-wire exactly equivalent to the two coils, it was deemed better not to attempt to alter the

cross-section by drawing or scraping, but to make the whole very slightly above  $\cdot 02$  ohm, and to reduce this to the desired exact value by inserting in the interior of the ebonite handle,



holding together the two U-pieces forming the movable slide-wire connexion, a small shunt of about 200 times the resistance of the wire. In case of subsequent alteration of the relation of the slide-wire resistance to that of the coils, this shunt could be altered as required, instead of a new slide-wire being necessary.

The blocks at the ends of the slide-wire, in addition to being firmly screwed, were connected to the bus-bars by mercury-cups and U-pieces, as it was not thought advisable to trust to the screws alone for a contact whose resistance must be negligible compared to  $\cdot 02$  ohm.

One great advantage of this form of instrument is that all the coils could be arranged so as to have their resistance adjusted, when in position in the box, by a method which could be made to include such of the contacts as were actually in circuit. The finest size of wire used will easily stand 1 ampere continuously through it; so adjustment even of the low coils to one part in a hundred thousand is not difficult.

The three sets of  $\cdot 01$  and  $\cdot 1$  ohm were made each of one continuous wire by selecting appropriate specimens of manganin, whose resistance from end to end was fairly uniform, and soldering to these by silver solder at equal distances short copper wires 1.5 mm. diam.

The whole was then bent to approximately the shape required, varnished with several coats of good shellac, and annealed by repeated heatings for some time to about  $140^{\circ}$  C.

The copper wires were then soft-soldered into place, the rough adjustment of the coils to about 1 part in 1000 being previously made by an appropriate method. After a week or two the fine adjustment was made by successive scraping, the contacts being employed as in actual use, and the whole being supported for this purpose at a convenient height by a suitable spider-frame.

When complete, two more coats of shellac were applied all over the interior of the box to protect against any possible inward leakage of mercury.

It is not of great importance that the coils of a potentiometer of this kind should be of negligible temperature-coefficient, so long as this is the same for all the different sizes of wire employed ; but it is desirable that the series-resistance, used to reduce the E.M.F. of the accumulator to that of the standard cell, should be of the same material as the potentiometer, so that the effect of temperature changes will be compensated. Placing the standard cells and also the accumulator in double-walled boxes packed with cork-clippings materially adds to the convenience of working, obviating the necessity for so frequently checking the compensating current.

Mercury reversing-keys in the circuit both of the battery and thermojunctions are a convenience, and where many junctions are in use together, it is better to have a larger selector-switch with multiple ways, instead of using the four-way one provided on the potentiometer proper.

All terminals of the potentiometer are arranged in one row at the back, and a cover over the box is provided, which, however, does not come over the terminals, so that the wires need not be detached when the instrument is not in use.

I am indebted for suggestions and help to Mr. Keeling,

and the making and adjustment of the coils of the instrument has been mainly done by Mr. Melsom, while the rest of the constructional work has been carried out very efficiently by the mechanic to the physical department, Mr. Murfitt.

Teddington, Feb. 1903.

#### DISCUSSION ON THE TWO FOREGOING PAPERS.

Mr. W. A. PRICE said that there was a great similarity between all forms of potentiometers. Electrically they were the same, but they differed mechanically. He referred to the small number of coils requiring calibration in the instruments exhibited. In working with sliding-contacts in a dusty workshop, it is an advantage to immerse the bridge in paraffin oil. The contacts are then always good, instead of uncertain and intermittent. He had also found that if two silver surface plates were screwed together, the contact-resistance was less when they were immersed in paraffin than when they were in air.

Mr. WHIPPLE said he had also found that contact-resistances in oil were less than in air. The oil acts as a lubricator, keeps the temperature constant, and the wires wear less.

Dr. WATSON said the effect of the oil seemed to depend upon the shape of the surfaces in contact, or it ought to be an advantage to grease the plugs of resistance-boxes. After what Mr. Price had said with regard to the contact-resistance of two pieces of silver, it would be interesting to work with a resistance-box in which the plugs were immersed in paraffin oil.

Prof. EVERETT expressed his interest in the fact that an insulating material, such as paraffin, should decrease the contact-resistance between two metals. He suggested that the paraffin drives off the film of air from the metals.

Dr. HARKER asked Dr. Lehfeldt if he had worked with all three sensitivities, and pointed out that the middle one was the same as that adopted in his own instrument.

Dr. LEHFELDT said that for small voltages he used the highest sensitivity. Inequalities in the slide-wire amounted to about  $\frac{1}{40}$  mm. of wire. The open scale in Dr. Harker's instrument was convenient in place of a vernier.

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XLVII. *Measurements of Small Resistances.**By* ALBERT CAMPBELL, B.A.\*

THE object of this paper is to give a brief account of a number of measurements of a set of low-resistance standards belonging to the National Physical Laboratory ; these tests were made partly with a view to comparing various methods of measurement, and it is from this point of view that they derive their main interest. The resistances were of the oil-cooled type and had separate potential terminals. They were made of manganin, and their nominal values were approximately 0.1, 0.01, and 0.001 international ohm respectively. For convenience of reference I shall allude to them as X, Y, and Z. Three other standard resistances of 1, 1, and 10 ohms, whose values have been accurately determined, formed the starting-point in each of the methods. Let them be named P, Q, and R respectively. The procedure was to find first the ratio of X to P, then that of Y to X, and, finally, that of Z to Y ; this gave X, Y, and Z in terms of P. The following methods were used :—

- (1) Shunt Potentiometer.
- (2) Kelvin Bridge.
- (3) Two-step Bridge.
- (4) Differential Galvanometer.
- (5) Matthiessen and Hockin's Method.

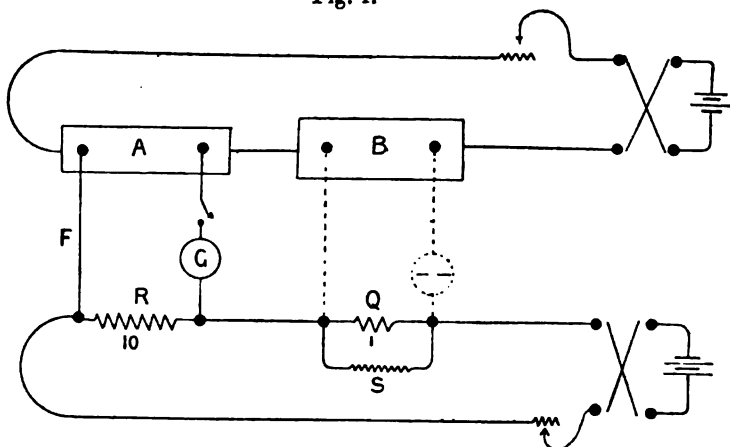
As most of these methods are well known I shall discuss each very briefly.

(1) *Shunt Potentiometer* —As shown in fig. 1 the potentiometer consisted of the known standards R and Q, one or other of them (say Q) being shunted by a high resistance S, while A and B were the resistances whose ratio was to be found. A special double key was arranged so that the cross-connexions (the wire F and the galvanometer G) could be quickly switched over from A and R to B and Q. The main current through A and B was kept constant, and the current through R and Q was adjusted till a balance was obtained in the first position (A against R). The switch was then turned

\* Read March 13, 1903.

to the second position, and  $Q$  was shunted so as to balance again, the process being repeated with successive adjustments until a balance was obtained in each position. To eliminate

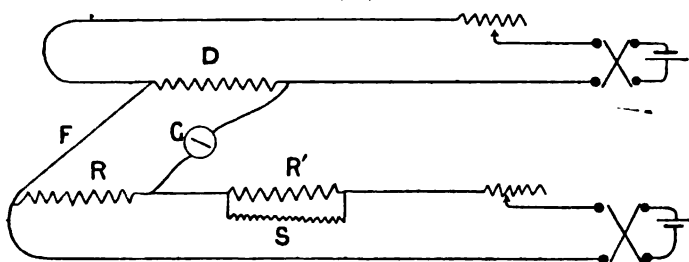
Fig. 1.



thermoelectric errors the two batteries were simultaneously reversed and the same process repeated ; from the mean value of  $S$ ,  $B$  was found in terms of  $A$ . The main advantage of the method lies in the simple and straightforward way of using the potential terminals, no current being taken from them when a balance is attained. The main defect is that large steady currents must be maintained, and this almost necessitates running the currents for a considerable time and altering the temperature of the coils.

In connexion with this I may mention the following simplification of the method, proposed by Mr. S. W. Melsom for

Fig. 2.

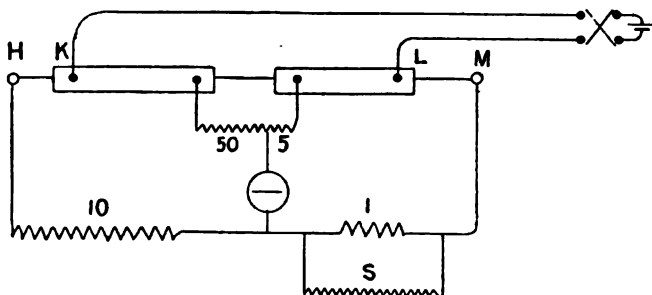


the purpose of comparing two nearly equal resistances. In fig. 2  $R$  and  $R'$  are the resistances to be compared, while  $D$

may be any unknown resistance of convenient magnitude. The double switch is arranged to switch the ends of F and G from R to R'. Thus a standard R can be copied at R' without the use of any other known resistances.

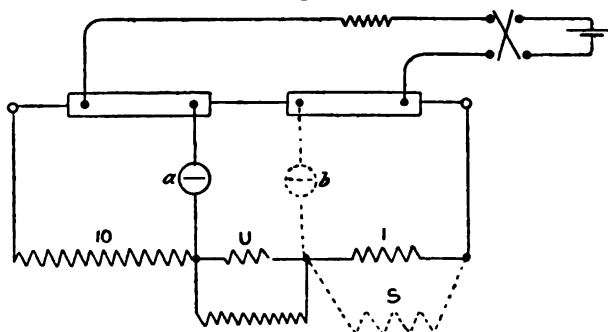
*Thomson Bridge.*—The setting up of this was similar to that used at the German Reichsanstalt, the connexions being

Fig. 3.



as in fig. 3. As the current entered and left by the potential leads at K and L, the leads HK and LM were included in the higher arms, and hence had to be measured. This was done with sufficient accuracy by passing a current through them, and measuring the potential-drop on the galvanometer. To eliminate thermoelectric effects the galvanometer circuit was kept closed, and the balancing was done by reversing the battery.

Fig. 4.



*"Two-Step" Bridge.*—This is shown in fig. 4. A suitable small resistance, whose value need not be known exactly, is inserted at U, and is adjusted by shunting until the galvano-

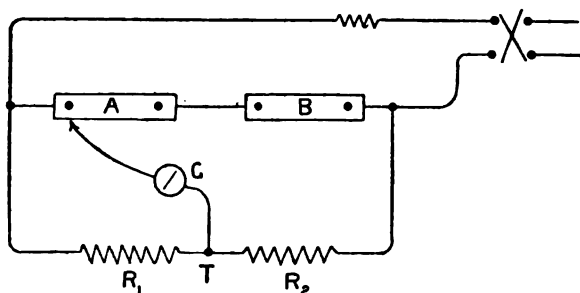


meter balances in position (*a*). The galvanometer is then brought into position (*b*), and a balance obtained by another shunt at *S*. With a suitable galvanometer this method is considerably more sensitive than the Thomson Bridge, but it is less convenient since it necessitates balancing twice.

*Differential Galvanometer.*—The method of using this is so well known\* that very little description is necessary. If the galvanometer circuits (100 ohms each) be called  $\alpha$  and  $\beta$ ,  $\alpha$  had in series with it a small adjustable resistance  $z$ , while in series with  $\beta$  was a non-inductive copper coil of 900 ohms. This coil was placed near the galvanometer, the whole being in a double-walled box lagged with wadding. The  $\alpha$  and  $\beta$  circuits were first connected in series and opposition, their magnetic effects on the needle being adjusted to balance in the usual manner by a small coil in series with one of them. Then, by adjusting  $z$ ,  $\alpha$  and  $\beta$  were set to balance on the 10 and 1 ohm coils. Without altering this adjustment a balance was now obtained on the coils (*A* and *B*) to be compared, by shunting one of them; and thus the ratio of *A* to *B* was determined. This method was only used for the 0.1 ohm coil, but it would have been equally convenient for the lower ones also.

*Matthiessen and Hockin's Method.*—The connexions are shown in fig. 5. By altering the resistances  $R_1$  and  $R_2$  a

Fig. 5.



balance was obtained with the galvanometer circuit connecting *T* with each of the potential points of *A* and *B* in

\* See Heaviside's Papers, vol. i.; also C. W. S. Crawley, Journ. Instn. of Electrical Engineers, April 1901.

succession. Let  $a, b, c, d$  be the respective values of  $\frac{R_1}{R_1 + R_2}$  for the four positions; then

$$\frac{A}{B} = \frac{b-a}{d-c}.$$

Although great care was taken to build up  $R_1$  and  $R_2$  from standard resistances, the method was found to be *much* less accurate than any of the four preceding ones. For example, the ratio of coil Y to coil Z was given as 10.0032 by one set of readings, and as 10.0057 by another. An examination of the formula shows that the degree of accuracy of the result may be much lower than that of the separate observations of  $a, b, c$ , and  $d$ .

In Table I. are given the collected results, the numbers being the observed resistances of the coils X, Y, and Z reduced to 17° C.

TABLE I.

Method.	X. Microhms.	Y. Microhms.	Z. Microhms.
(1) Potentiometer .....	100007	100013 <sub>7</sub>	99994 <sub>7</sub>
(2) Thomson Bridge .....	100005 <sub>2</sub>	100012 <sub>2</sub>	99997 <sub>2</sub>
(3) Two-step „ .....	100005 <sub>3</sub>	100012 <sub>3</sub>	99998 <sub>4</sub>
(4) Differential Galvanometer	100007 <sub>4</sub>	—	—

In Table II. are given the corresponding sensitivities expressed in galvanometer scale-divisions (1 mm. at 1000 mm.) for 1 part in 100,000.

TABLE II.

Method.	X.	Y.	Z.
(1) .....	0.7	0.6	0.4
(2) .....	0.8	0.8	0.28
(3) .....	1.2	1.2	0.42
(4) .....	0.3	—	—

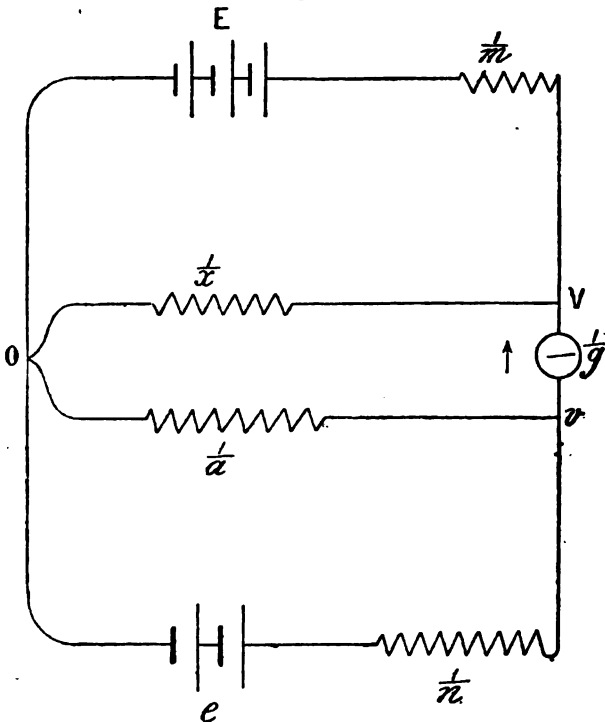
In conclusion I may remark that, within the limits of accuracy indicated by the numbers in Table II., the results given in Table I. show satisfactory agreement.

## APPENDIX.

*On the Sensitivity of Potentiometers for Measuring Resistance.*

To obtain the best results with a potentiometer it is usually desirable that it should be of such resistance as to give, with the available galvanometer, the maximum sensitivity. If several galvanometers are available, it is important to have a means of predicting which will be the most suitable in any particular case. I have therefore investigated the general formula for the sensitivity of a potentiometer when used for measuring resistances with a galvanometer of given resistance, extending it to the more general case by the common assumption that the "current-sensitivity" of a galvanometer is proportional to the square root of its resistance.

Fig. 6.



In fig. 6 let the resistances have the values shown, viz.  $\frac{1}{a}, \frac{1}{n}$ ,

$\frac{1}{x}$ ,  $\frac{1}{m}$ , and  $\frac{1}{g}$ ;  $\frac{1}{m}$  and  $\frac{1}{n}$  including the resistances of the adjacent batteries whose E.M.F.'s are  $E$  and  $e$  respectively. Let  $0$ ,  $V$ , and  $v$  be the potentials at the points so marked. Let  $c$  = current through galvanometer, so that  $c = (v - V)g$ .

$\frac{1}{a}$  is the part of the circuit under test, while  $\frac{1}{x}$  is the part of the potentiometer in use.

We have

$$(V - E)m + Vx = (v - V)g = -(v - e)n - va.$$

Hence

$$(m + x)V - c = mE,$$

and

$$g(a + n)V + (g + a + n)c = gne;$$

$$\therefore c = \frac{gnex + gmn(e - E) - gamE}{(g + a + n)x + (m + g)(a + n) + mg}.$$

The sensitivity

$$\begin{aligned} &= \left[ \frac{\Delta c}{\Delta x} \right]_{c=0} = - \left[ x \frac{\partial c}{\partial x} \right]_{c=0} \\ &= - \frac{gnex}{(g + a + n)x + (m + g)(a + n) + mg} = -\sigma \text{ (say).} \end{aligned}$$

When  $c = 0$ ,

$$nex + mn(e - E) - amE = 0;$$

$$\therefore m = \frac{nex}{(n + a)E - ne};$$

$$\therefore \sigma = \frac{gnex}{(g + a + n) \left[ x + \frac{nex}{(n + a)E - ne} \right] + (a + n)g}$$

Let resistances be written instead of conductances, i. e. let  $\frac{1}{x} = X$ ,  $\frac{1}{m} = M$ , &c. Also let  $k = A/N$ .

Then

$$\sigma = \frac{ke}{1 + k} \cdot \frac{1}{[A + G(1 + k)] \frac{E}{(1 + k)E - ke} + X} \dots (1)$$

This is the complete formula.

If  $e = E$ , it takes the simple form

$$\sigma = \frac{kE}{1+k} \cdot \frac{1}{A+X+G(1+k)} \quad \dots \quad (2)$$

It can be seen from (1) that since  $k$  is always positive,  $G$  has always more relative influence than  $X$ .

When the galvanometer resistance has not been fixed, if we make the usual assumption mentioned above, then the sensitivity is proportional to  $\sigma \sqrt{G}$ , and can be calculated for any case. The following table shows the result in two, possibly extreme, cases (when  $E = e$ ).

TABLE.

$k$ .	$G$ .	$A$ .	$X$ .	$\sigma$ varies as	$\sigma \sqrt{G}$ varies as
0.1	100	0.01	100	$\frac{1}{2100}$	$\frac{1}{210}$
0.1	1	0.01	0.1	$\frac{1}{22}$	$\frac{1}{12.1}$

The values of  $\sigma \sqrt{G}$  show that for measuring a potential-drop on a resistance of 0.01 ohm (with the battery voltage eleven times the voltage measured) a potentiometer of 0.1 ohm and galvanometer of 1 ohm give nearly twenty times greater sensitivity than a potentiometer and galvanometer of 100 ohms each.

This example is sufficient to indicate the importance of choosing the resistances suitably.

At the same time it should be remarked that in several ways the low-resistance potentiometer is less easy to construct and work; for instance, it may require much larger steady currents; and these practical considerations may sometimes outweigh the advantages of greater sensitivity.

XLVIII. *On Refraction at a Cylindrical Surface.*

By ARTHUR WHITWELL, M.A., A.R.C.Sc.I.\*

[Plate VIII.]

THE object of this paper is to describe and illustrate the position and form of the focal areas produced by the refraction at a cylindrical surface, bounding two media of different refractive indices, of light diverging from or converging to a point.

In general, when light diverging from or converging to a point falls on any surface bounding two media of different refractive indices, if a plane can be drawn through the point to cut an element of, or the whole surface, symmetrically, then all the light will really or virtually pass through a focal line or focal area in this plane. It is usual, when considering elements of the surface only, to use the term focal line, but it should always be remembered that these focal lines are in general elements of area. In the case we are about to consider there are two planes, about which the surface is symmetrical, which can be drawn through the radiant-point. One of these planes will contain the axis of the cylinder, and the other will be normal thereto.

We will consider first the plane containing the radiant-point and the axis of the cylinder.

Let fig. 1 (Pl. VIII.) be a plan and elevation of the cylinder of radius  $r$ , and let the radiant-point  $o$  be at a distance  $a$  from the axis. Draw the elevations and plans of two symmetrical incident rays and of the corresponding normals and refracted rays, join  $oc$  and produce to meet the refracted ray in a point  $g$ . The two refracted rays will meet at the point  $g$ , and the locus of the point  $g$  will be the focal line. A plane containing the points  $o, a, c$  will contain an incident ray and the normal, and will therefore also contain the corresponding refracted ray. This plane will cut the plane of the figure (1) in the line  $ocg$ , and the refracted ray will in general cut this line  $ocg$  in some point  $g$ . Again, a plane containing the points  $o, b, c$  will contain the corresponding symmetrical

\* Read March 27, 1903.

incident ray, normal, and refracted ray, and will cut the plane of the figure in the line  $ocg$ . From considerations of symmetry it follows that the two refracted rays will intersect in the same point  $g$  on the line  $ocg$ . If we consider only a thin slice of the cylinder parallel to the plane of the paper in fig. 1, the elevations of the lines  $oa$ ,  $ac$ , and  $ag$  may be taken as their true lengths.

Let the vertical aperture =  $h$ ,  
 The angle of incidence =  $\theta$ ,  
 „ of refraction =  $\phi$ ,  
 „  $agc$  =  $\beta$ ,  
 „  $com$  =  $\psi$ ,  
 and the length  $cg$  =  $d$ .

Then we have

$$\begin{aligned}\beta &= \psi - \phi \\ \sin \theta &= \mu \sin \phi \\ d \sin \beta &= r \sin \phi \\ d &= \frac{r \sqrt{a^2 + h^2}}{h \cot \phi - a},\end{aligned}$$

from which we get

$$d = \frac{r \sqrt{a^2 + h^2}}{\sqrt{\mu^2(a-r)^2 + (\mu^2 - 1)h^2} - a}. \quad \dots (1)$$

Taking the radiant-point as origin, the equation to the locus is

$$x = a + d \cos \psi,$$

or

$$x = a + \frac{ra}{\sqrt{\mu^2(a-r)^2 + (\mu^2 - 1)h^2} - a},$$

and putting in the value of

$$h = \frac{ay}{x},$$

we get finally

$$y^2 = \frac{x^2}{a^2(\mu^2 - 1)} \left\{ \frac{(ax + ra - a^2)^2 - (\mu(a-r)(x-a))^2}{(x-a)^2} \right\}. \quad (2)$$

It may be stated here that the equation represents not only the locus of the intersections of the real refracted rays, but also of the false refracted rays. These false rays are equally inclined to but on the opposite side of the normal to the real

rays. This arises from the fact that we have to square to get rid of the radical sign in the denominator of the expression for  $d$ ; for this reason it is immaterial, as far as the equation arrived at is concerned, whether we take the + or — sign before the radical quantity in the denominator of  $d$ .

The curves represented by this equation, taking  $\mu = \frac{3}{2}$  and  $r = 2$  and various values of  $a$ , are shown plotted in fig. 4, the light proceeding from left to right. When the radiant-point is at infinity, the focal line will be the straight line I. at a distance  $\frac{\mu r}{\mu - 1}$  from the surface, or  $\frac{r}{\mu - 1}$  from the axis of the cylinder. As the radiant-point moves up to the surface, the focal line gradually bulges out to the right at its centre, and its upper and lower ends bend towards and become asymptotic to the axis as shown by curve II., for which  $a = 10$ . When the distance of the radiant-point from the surface  $= \frac{r}{\mu - 1}$ , or when  $a = \frac{\mu r}{\mu - 1}$ , the centre of the focal line breaks, and its two ends become parallel to, but at an infinite distance from, the axis of  $x$ . The curve III. has parabolic asymptotes, the equation of which, referred to the radiant-point as origin, is

$$y^2 = 3 \cdot 2 x + 22 \cdot 4.$$

This point,  $a = \frac{\mu r}{\mu - 1}$ , will be recognized as the principal focus for light proceeding from right to left. When the radiant-point is inside this focus, the curve, IV., has two branches and a pair of rectilinear asymptotes, the axis of the cylinder remaining an asymptote. The branch on the left is of course virtual.

As the radiant-point moves to the right, the angle which the rectilinear asymptote makes with the axis of  $x$  increases from zero to a maximum, and then diminishes to zero. When the radiant-point is on the surface there is no focal line; an incident cone of light produces a refracted cone, the ratio of the sines of the semi-angles of the cones being  $= \mu$ .

I have not plotted the false focal lines in curves I.-IV.; they all lie between the surface of the cylinder and the axis, to which they are asymptotic.



When  $a$  lies between  $r$  and  $\frac{\mu r}{\mu+1}$ , the real focal line lies between the surface and axis of the cylinder, and the false focal line has two branches and a pair of rectilineal asymptotes.

When  $a = \frac{\mu r}{\mu+1}$  the real line is shown by curve V., and the false line has parabolic asymptotes, the equation of which is

$$y^2 = 3 \cdot 2x + 7.$$

A graphical method of drawing the asymptotes may be obtained by considering equation (1),

$$d = \frac{r\sqrt{a^2 + h^2}}{\sqrt{\mu^2(a-r)^2 + (\mu^2-1)h^2} - a}.$$

If  $\mu^2(a-r)^2 + (\mu^2-1)h^2 = a^2$ ,  $d$  is infinite, and this relation between  $a$  and  $h$  gives us the circle shown in fig. 4.

To obtain the asymptotes, draw an ordinate to the circle through the radiant-point, and project horizontally to a point on the axis of the cylinder. The asymptote will pass through this point on the axis, and through the radiant-point. When  $a=0$  the focal line will be the axis itself, and this is the only case in which the focal line will be a mathematical straight line whether the aperture be large or small.

When  $a$  becomes negative the curve is still asymptotic to the axis (see curve VI., for which  $a=-10$ ), and as  $a$  increases the curve gradually moves to the right and approaches the line I., which it reaches when  $a$  is infinite.

The set of curves shown in fig. 5 are for the case in which light proceeds from a denser to a rarer medium, and are obtained by putting  $\mu = \frac{2}{3}$  in equation (2).

When the radiant-point is at infinity the focal line is a straight line, VII., at a distance  $\frac{r}{\mu-1}$  from the surface, or  $\frac{\mu r}{\mu-1}$  from the axis: it is virtual. As the radiant-point moves to the right, the curve becomes of the form shown by VIII., for which  $a=10$ . In this curve, when the vertical aperture  $h = \pm \frac{\mu(a-r)}{\sqrt{1-\mu^2}}$ , total reflexion occurs, and the focal line cuts the surface; the continuation of the curve inside the cylinder is the false focal line.

As  $a$  diminishes, the curve becomes smaller (curve IX. is for  $a=6$ ), and finally diminishes to a point when  $a=r$ ; in this case a cone of light having a semi-vertical angle equal to the critical angle is refracted, the remainder of the incident light being totally reflected, and the refracted cone having a semi-angle of  $\frac{\pi}{2}$ . When the radiant-point is inside the cylinder, or when the light is convergent, the curve becomes of the form X., for which  $a=1$ . In this case the part of the curve inside the cylinder is the real, and the part outside the false focal line.

When  $a = \frac{\mu r}{\mu + 1}$  the curve, XI., has parabolic asymptotes, the equation of which is

$$y^2 = -7.2x - 13.$$

When  $a$  lies between  $\frac{\mu r}{\mu + 1}$  and  $\frac{\mu r}{\mu - 1}$  the curve has two branches and a pair of rectilinear asymptotes. Curve XII. is for  $a=5$ , and the branch on the right and that part of the branch on the left which is outside the cylinder are the false focal line, the real focal line being that part of the left branch which is inside the cylinder. The asymptotes may be drawn by means of a circle, the equation of which is obtained as before.

When  $a=0$ , the axis is the focal line. When  $a$  lies between 0 and  $\frac{\mu r}{\mu - 1}$  or  $-4$ , the curve has two branches; the branch on the right and that part of the branch on the left which is outside the cylinder are the real focal line, and that part of the branch on the left which is inside the surface is the false focal line.

When  $a=-4$ , the curve, XIII., has parabolic asymptotes, the equation of which is

$$y^2 = -7.2x + 21,$$

this point being the principal focus for rays passing from right to left.

When  $a$  is negative and greater than 4 the curve has only one branch, which lies on the left of the axis, that part outside

the surface being the real and that part inside the false focal line. Curve XIV. is for  $a = -10$ .

As the radiant-point moves off to infinity towards the right, the curve approaches and ultimately coincides with the straight line VII.

The curves shown in figs. 4 and 5 are for light falling on the convex surface of the cylinder, but by reversing them about the axis of the cylinder they will represent the focal lines produced by light passing from left to right and falling on the concave surface of the cylinder if the corresponding values of  $a$  be also reversed in sign.

We shall now find the equation of the locus of the intersection of two symmetrical rays which have the greatest angle of incidence possible, viz.  $\frac{\pi}{2}$ . Suppose the triangle *oag*, fig. 1, to be turned down into the plane of the paper on the line *og*, as shown in fig. 2. We know that

$$oc = \sqrt{a^2 + h^2}; \quad oa = \sqrt{a^2 - r^2 + h^2}; \quad \theta = \frac{\pi}{2};$$

and that 
$$\sin \phi = \frac{1}{\mu}.$$

We also have 
$$r \sin \phi = d \sin \beta,$$

$$d = \frac{r}{\mu \sin \beta} = \frac{r \sqrt{a^2 + h^2}}{\sqrt{\mu^2 - 1} \sqrt{a^2 - r^2 + h^2} - r}. \quad (3)$$

Taking the radiant-point as origin,  $x = a + d \cos \psi$ , or

$$x = a + \frac{ra}{\sqrt{\mu^2 - 1} \sqrt{a^2 - r^2 + h^2} - r},$$

and putting  $h = \frac{ay}{x}$ , the equation reduces to

$$y^2 = \frac{x^2}{a^2(\mu^2 - 1)} \left\{ \frac{x^2 r^2 - (\mu^2 - 1)(a^2 - r^2)(x - a)^2}{(x - a)^2} \right\} \quad (4)$$

Putting  $\mu = \frac{3}{2}$ ,  $r = 2$ , the locus represented by this equation is shown plotted in fig. 6. The general nature of the curves is the same as that of the curves for small apertures shown

by fig. 4. As before, we can get a relation between  $a$  and  $h$  for which the corresponding value of  $d$  is infinite.

In this case  $d = \infty$  when  $a^2 + h^2 = \frac{\mu^2 r^2}{\mu^2 - 1}$ ; this relation represents a circle of radius  $= \frac{\mu r}{\sqrt{\mu^2 - 1}}$ .

When  $a = \infty$  the focal line is a straight line, XV., at a distance  $\frac{r}{\sqrt{\mu^2 - 1}}$  or 1.78 from the axis. As the radiant-point moves to the right, the curve bulges out at the centre and bends towards the axis at each end, as shown by curves XVI. and XVII., for which  $a = 10$  and  $a = 4$ .

When  $a = \frac{\mu r}{\sqrt{\mu^2 - 1}} = 2.68$ , the principal focus for rays going from right to left, the curve, XVIII., has parabolic asymptotes.

When  $a$  lies between  $\frac{\mu r}{\sqrt{\mu^2 - 1}}$  and  $r$ , or between  $\frac{-\mu r}{\sqrt{\mu^2 - 1}}$  and  $-r$ , the curve has three branches and a pair of rectilinear asymptotes. Curve XIX. is for  $a = 2.4$ ; the false focal line is not drawn, and the branch on the left is virtual.

When  $a$  lies between  $r$  and  $-r$ , we cannot have an angle of incidence of  $\frac{\pi}{2}$ .

When  $a$  lies between  $-r$  and  $-\frac{\mu r}{\sqrt{\mu^2 - 1}}$  we get a curve like XIX., but reversed about the axis of  $y$ . As the radiant-point moves to the right, the focal line gradually approaches and finally coincides with the line XV. (See curve XX., which is for  $a = -10$ .)

When the light passes from a denser to a rarer medium we cannot obtain the equation of the locus of the intersection of symmetrical refracted rays by putting  $\mu$  less than unity in equation (4), because for an angle of incidence of  $\frac{\pi}{2}$  the rays would be totally reflected. The maximum angle of incidence will be the critical angle; we shall, therefore, find the equation of the locus for symmetrical rays having an angle of incidence the sine of which  $= \frac{1}{\mu}$ . When the triangle  $oag$  is folded down into the vertical plane on the line  $og$ , we shall get the construction shown in fig. 3, in which  $\theta$  is the angle

of incidence,  $\phi$  the angle of refraction. We have

$$\sin \theta = \mu; \beta = \theta - \alpha; r \sin \theta = \sqrt{a^2 + h^2} \sin \alpha; d = \frac{r}{\cos \beta},$$

$$\text{or} \quad d = \frac{r \sqrt{a^2 + h^2}}{\sqrt{1 - \mu^2} \sqrt{a^2 + h^2 - \mu^2 r^2} + \mu^2 r} \quad \dots (5)$$

$$x = a - d \cos \psi,$$

and putting  $h = \frac{ay}{x}$  we get finally

$$y^2 = \frac{x^2}{a^2(1 - \mu^2)} \left[ \frac{(\mu^2 ra - ra - \mu^2 rx)^2 - \{(x - a)^2(1 - \mu^2)(a^2 - \mu^2 r^2)\}}{(x - a)^2} \right].$$

The locus represented by this equation is shown plotted in fig. 7,  $r$  being  $= 2$  and  $\mu = \frac{2}{3}$ .

The equation to the circle which gives the asymptotes is

$$a^2 + h^2 = \frac{\mu^2 r^2}{1 - \mu^2}.$$

When  $a = \infty$  the focal line is the straight line XXI. at a distance  $\frac{r}{\sqrt{1 - \mu^2}}$  or 2.68 from the axis. As the radiant-point moves to the right the focal line also moves to the right and becomes asymptotic to the axis, as shown by curve XXII. for which  $a = 10$ . The branch of the curve XXII. on the right is the focal line for light falling on the concave surface. The real and false focal lines coincide since the refracted ray is at right angles to the normal at the point of incidence. The parts of the curves inside the cylinder have no real existence, they are the loci of intersection supposing that total reflexion did not occur. As the radiant-point approaches the surface the real portion of the focal line becomes shorter and dwindles to zero when the radiant-point reaches the surface. Curve XXIII. is for  $a = \frac{\mu r}{\sqrt{1 - \mu^2}}$  or 1.78, which is the point where the asymptote circle cuts the axis of  $x$ ; the branch on the left, of which only a minute portion is real, is the focal line for light falling on the convex surface of the cylinder, and the branch on the right, which has parabolic asymptotes, is the focal line for light falling on the concave surface of the cylinder.

Curve XXIV. is for  $a=1.33$ . The branch on the right and the left-hand part of the branch on the left above the axis of  $x$  is the focal line for light falling on the concave part of the cylinder, whilst the remainder of the left-hand branch is the focal line for light falling on the convex portion of the cylinder. When  $a=0$  the axis is the focal line, when  $a$  is negative the curves are got by reversing the corresponding curves for positive values of  $a$ . Thus curve XXV., which is curve XXII. reversed, is for  $a=-10$ .

As the radiant-point moves off to the right the focal line gradually approaches and ultimately coincides with the line XXI. from which we started.

We have now plotted the focal lines for maximum and minimum horizontal aperture in all possible cases. A curve from fig. 4 or fig. 5 and the corresponding curve from fig. 6 or fig. 7, *e.g.* curves IV. and XVII., will define the focal area, that is to say, all the light from the corresponding radiant-point will after refraction pass through the area between these curves. If we suppose ourselves at the radiant-point and facing the cylinder half the light will be bent from left to right and the other half from right to left, but it will all pass through the central plane containing the radiant-point and the axis, in the area between these two curves. It is easily seen that the width of the focal area on the axis of  $x$  will be equal to the spherical aberration of the section of the cylinder made by a horizontal plane containing the axis of  $x$ .

We will now consider the focal areas produced in the second symmetrical plane, *viz.*: the plane containing the radiant-point and normal to the axis of the cylinder. Draw a similar construction to that shown in fig. 1 for two rays symmetrical with regard to the horizontal plane, and produce the refracted rays backwards till they intersect at the point  $k$  in the horizontal plane. This point  $k$  will be on a straight line drawn through the radiant-point and parallel to the two normals.

Consider, first, a thin horizontal slice of the cylinder containing the axis of  $x$ . For small horizontal aperture the

distance  $cf = \frac{ra}{(\mu-1)a-\mu r}$ . By small apertures I mean those for which one can neglect the spherical aberration in comparison with the length  $cf$ .

Let

$$cf=c, \text{ and } ok=d'.$$

Then from the figure we have

$$\frac{c}{a+c} = \frac{r}{d'}$$

$$d' = \frac{r(a+c)}{c} = (\mu-1)(a-r).$$

For small horizontal apertures then the focal line is an arc of a circle having its centre at the radiant-point and its radius  $d' = (\mu-1)$  times the distance of the radiant-point from the surface. The focal line is virtual for diverging light and real for converging light. If we take two horizontal strips of the cylinder at a distance of  $h$  above and below the horizontal plane the focal line formed by rays which fall on these two strips will also be a circular arc for small horizontal apertures. Its radius  $d''$  is obtained from the relation

$$\frac{d}{\sqrt{a^2+h^2}} = \frac{r}{d''}$$

$$d'' = \frac{r\sqrt{a^2+h^2}}{d} = \sqrt{\mu^2(a-r)^2 + (\mu^2-1)h^2} - a.$$

All the light which falls on the cylinder will therefore virtually pass through the area in the horizontal plane between arcs of two circles of radius  $d'$  and  $d''$  having the radiant-point as centre. The width of the focal area on the axis of  $x = d'' - d'$  and this width increases as the vertical aperture  $h$  increases, and becomes infinite when  $h$  is infinite.

The focal lines or areas we have discussed are produced by the intersections of symmetrical rays. Besides these the refracted rays produce two caustics which are the loci of intersections of consecutive rays. The first is the locus of the intersections of consecutive refracted rays in the plane containing the radiant-point and the axis of the cylinder, and is the same as that which would be produced by rays in one plane refracted at a plane surface dividing any two media of

different refractive indices. The second is the locus of the intersections of consecutive refracted rays in the plane containing the radiant-point and normal to the axis of the cylinder, and is the caustic of the circle. Incident rays in oblique sections of the cylinder do not produce caustics since the corresponding refracted rays are not in the same plane.

If we suppose light from a radiant-point to fall on a cylinder the radius of which gradually increases to infinity, it will be seen that ultimately, when the curvature is zero, the two focal areas will coincide and be reduced to a short piece of the line through the radiant-point and normal to the surface. Similarly, if we suppose the cylinder to become a semi-ellipsoid which gradually becomes a hemisphere, then the two focal areas will ultimately coincide and become a portion of the line joining the radiant-point and the centre of the hemisphere.

Instead of having caustics in two planes only we now have a caustic in every plane passing through the radiant-point and the centre of the hemisphere.

If light proceeding from or to a point  $a$  fall on the plane or spherical surface of a plano- or spherocylindrical lens of small aperture it will pass on to the cylindrical surface as if it proceeded from a point  $a'$ ,  $a$  and  $a'$  being conjugate with respect to the first surface. The focal areas produced by a plano- or spherocylindrical lens are therefore, for small apertures, identical with those produced by refraction at a single cylindrical surface; and if we define two optical systems as "equivalent" when they produce identical focal areas, then we can say that a plano- or spherocylindrical lens with the radiant-point at  $a$  is equivalent to a single cylindrical surface with the radiant-point at  $a'$ ;  $a$  and  $a'$  being conjugate with respect to the first surface.

In conclusion, I should like to call attention to a misleading statement made by Prof. S. P. Thompson, in a paper on this subject read before this Society on December 8th, 1899\*. He says:—"In any lens having at one surface a radius of curvature  $r$ , the curvature which that surface will impress upon a plane wave is  $\frac{\mu-1}{r}$ ; where  $\mu$  is the refractive index

\* Phil. Mag. March 1900; Proc. Physical Soc. vol. xvii. p. 81.



of the material. If the lens is cylindrical, having a curvature in one meridian only, the impressed curvature will also be cylindrical."

"Let  $AA'$  be the axis of a cylindrical lens, and  $NN'$  a line normal to that axis. A plane normal to the axis intersecting the lens in  $NN'$  will have as its trace through the curved surface of the lens a line of the same curvature as the lens, viz.  $\frac{1}{r}$ . Let now an oblique intersecting plane be drawn through the optic axis of the system; its intersection  $PP'$  making an angle  $NOP = \phi$  with the line  $NN'$ . The curvature at  $O$  of the trace of this plane, where it cuts the curved surface along  $PP'$ , will be  $\frac{1}{r} \cos^2 \phi$ .... We may further consider the intersection  $QQ'$  of another oblique plane at right-angles to  $PP'$ . The curvature at  $O$  along the line  $QQ'$  will be  $\frac{1}{r} \sin^2 \phi$ .... If light were admitted through narrow parallel slits set respectively along  $PP'$  and  $QQ'$ , the convergivity of the two beams respectively impressed by the lens would be  $(\mu-1) \frac{\cos^2 \phi}{r}$  and  $(\mu-1) \frac{\sin^2 \phi}{r}$ . If  $r$  is expressed in metres, then these two convergivities will be expressed in dioptries...."

Now if a plane wave fall on a thin plano-cylindrical lens the emergent wave-surface, for small aperture, will be a cylinder of radius  $\frac{r}{\mu-1}$ . Every refracted ray will pass through a line or narrow band parallel to the axis of the cylinder and at a distance  $\frac{r}{\mu-1}$  from the lens. If we suppose a card with a narrow diagonal slit to be placed in front of the lens it is obvious that a great part of the cylindrical wave-surface will be cut off, but the portion that remains will still be cylindrical, and will have the same radius. The rays that pass through the slit still pass through the line at the distance  $\frac{r}{\mu-1}$ , and the convergivity is the same as before. The power of impressing convergence on a plane wave of the diagonal strip of the lens is the same as the power of the whole surface. A cylindrical lens can only properly be held

to have *two* powers, and it appears to me to be a mistake to speak of the power of a cylindrical lens along a line making an angle  $\phi$  with the axis as being  $\frac{\mu-1}{r} \sin^2 \phi$ .

If parallel light be allowed to fall on a cylindrical lens and a ground-glass screen be placed at a distance of  $\frac{r}{\mu-1}$  from the lens, then a line of images of the source of light, parallel to the axis of the cylinder, is seen on the screen. If a stop with a diagonal slit be now inserted and the screen be moved up close to the lens, a line of images out of focus, less intense than before, and parallel to the slit is seen on the screen; as the screen is moved away this line of images rotates and gradually becomes sharper, until when at length the screen reaches the distance  $\frac{r}{\mu-1}$  the line of images is parallel to the axis of the cylinder and is perfectly sharp. This shows that the slit has made no difference to the position of the focus or to the power of the lens. As the screen moves further back still, the line of images continues to rotate in the same direction and gets more and more fuzzy or out of focus.

In a paper entitled "On Astigmatic Lenses," read before this Society on November 9th, 1900\*, Mr. R. J. Sowter makes the same mistake, and speaks of the power of a cylindrical lens in a direction OR making an angle  $\phi$  with the axis of the lens as  $A \sin^2 \phi$ , where A is "the equatorial or focal power of the lens." He also speaks of the power of a plano-ellipsoidal lens along a direction OR making an angle  $\phi$  with an axis of the elliptic plane face of the lens as being  $= A \cos^2 \phi + B \sin^2 \phi$ , A and B being the two powers of the lens.

My remarks apply as well to an ellipsoidal lens as to a cylindrical. When the radiant-point is on an axis of an ellipsoidal lens, the light produces two focal areas and two caustics in the planes of maximum and minimum curvature. A thin slice of the lens parallel to the direction OR will not produce caustics, and the rays which pass through it will all pass through the same focal areas as they would if the whole

\* Phil. Mag. Feb. 1901; Proc. Physical Soc. vol. xvii. p. 553.

lens were employed. A screen placed at distances  $\frac{1}{A}$  or  $\frac{1}{B}$  would show the same sharp but less intense lines of images of the source of light as when the whole lens was used.

Both of these writers appear to have considered the curvature of the section of the lens in any direction to be the important element in determining the position of the focal lines instead of the principle of symmetry.

I have to thank Prof. Everett for suggesting to me the reason why my equations represent the false focal lines as well as the real; also Mr. Lyndon Bolton for tracing the curve represented by equation (2), and showing that in a particular case it has parabolic asymptotes.

#### DISCUSSION.

Prof. EVERETT said he had had an opportunity of studying the paper and found the reasoning sound. He was pleased that the author had treated focal lines rigorously, and not assumed them to be perpendicular to the axis of the pencil. The focal lines discussed in the paper were the secondary lines. The primary lines were only mentioned casually near the end under the name of caustics. The "false lines" given by the equations arose from negative values of a square root which ought to be taken positively.

As regards oblique sections of an astigmatic lens, he agreed with Mr. Whitwell that there was no proper focussing except in the two principal planes; nevertheless it was useful to discuss the distance at which the best image of an obliquely placed line was formed: and this distance was correctly given by the statements which had been criticised.

Dr. R. T. GLAZEBROOK said he agreed with Prof. Everett in his remarks concerning the rigorous treatment of the focal lines.

**XLIX.** *Note on the Construction and Attachment of Thin Galvanometer Mirrors.* By W. WATSON, D.Sc., F.R.S., Assistant Professor of Physics, Royal College of Science, London\*.

As has been pointed out by several persons (Rayleigh, Phil. Mag. xx. p. 360, 1885; Threlfall, Proc. Phys. Soc. xvi. p. 205, 1898) there are distinct advantages in increasing the sensitiveness of the optical arrangements used to measure the rotation of a galvanometer needle rather than increasing the electrical sensitiveness, *i.e.* the angular deflexion produced by a given small current. Excessive electrical sensitiveness implies a very weak controlling force. Such a weak controlling force involves a long period, and also disturbances produced by convection currents in the air and tremors in the supports of the instrument.

In order to increase the optical sensitiveness of a galvanometer it is necessary to increase the diameter of the mirror, while, to allow of its being carried by a fine suspension and to keep the period low, the weight of the mirror must be made as small as possible, yet at the same time its figure must remain good. With the ordinary form of mirror, consisting of a disk of glass silvered on the back, it is almost impossible to obtain a really thin mirror with a good figure unless the area of the mirror is excessively small. In the first place, the grinding and polishing of a very thin slip of glass is an operation which taxes the skill of the optician to the utmost. More important, however, is the fact that the silver backing of the mirror has to be coated with some kind of varnish to protect the silver from the action of the impurities in the air. Although numberless kinds of varnish have been tried for this purpose none has yet been discovered which does not distort the mirror to some extent. A further difficulty in the case of the glass mirror is the attachment of the mirror to the stem which carries the magnets, the cement employed almost always producing some distortion. While designing

\* Read May 8, 1903.

a special form of mirror for use in a magnetograph I have been led to a method of constructing galvanometer mirrors which I believe entirely obviates the difficulties mentioned above.

Prof. Threlfall has already pointed out the advantages of quartz as a material from which to construct galvanometer mirrors, but he, I believe, employed silvered mirrors, and hence had to use some form of varnish, and also he cemented the mirrors to the rod which carried the magnets. He tried both crystalline quartz and fused silica, and states he found them equally suitable. In my case I was obliged to use fused silica, and when I attempted to use thin slices silvered on the back I found that there was a very considerable loss of light owing to the small bubbles which are always present in any but the smallest pieces of fused silica. It then occurred to me to try and use some material for the reflecting surface which would be unaffected by the air. Platinum naturally was the material first tried, and after testing practically all the methods of which I could hear for giving a bright film of platinum, I obtained from Messrs. Johnson and Matthey a platinizing solution which is entirely satisfactory, and gives without any polishing a perfectly bright surface of platinum. The film of platinum obtained is bright on the surface turned away from the silica, so that the reflexion takes place at the air-platinum surface, and hence the silica disk requires polishing on one surface only, a circumstance which, as will be seen, very much simplifies the construction of thin mirrors.

The method I adopt for making the mirrors is as follows:—A stick of fused silica is prepared having a diameter equal to the diameter of the mirror it is wished to prepare. This stick is cemented to a small piece of wood by means of pitch. A disk of tinned iron (No. 28, s.w.g.) about 12 centimetres in diameter is mounted on a mandrel and the edge turned true. A little diamond-dust mixed with thick oil is then spread round the edge of the disk, and while rotating the disk at the rate of about five turns a minute a piece of flint is pressed firmly against the edge. In this way the diamond particles are driven into the iron and, at any rate after an attempt or two, the disk will be satisfactorily armed. A

horizontal plate with a guide at one edge is attached to the slide-rest of the lathe and the wooden base to which the silica is attached is placed on this plate, and the silica pressed firmly against the edge of the disk which is rapidly rotated. Soap and water must be used as a lubricant, being supplied by means of a brush. In this way a disk having a diameter of one centimetre can be cut in a minute.

A small rod of fused silica is then fused to the edge of the disk by means of a small oxyhydrogen flame, and all but the last two or three millimetres cut off, so as to leave a small tag of silica. The disk is then roughly ground flat on either side by rubbing it on a flat plate of brass freely supplied with powdered carborundum (of such a size as to pass through a sieve of 250 threads to the inch) and water. The disk is then annealed by being heated to a bright red in a small scoop of platinum or thin sheet-iron over a Bunsen flame for about 5 hours. That surface of the disk which, on inspection, appears most free from bubbles is ground on a plate of thick plate-glass with water and emery of gradually increasing fineness. The disk is moved round and round in circular sweeps, the end of the finger pressing it lightly down on the surface of the glass. About ten minutes' grinding with each of three grades of washed emery, finishing with the finest which can be obtained, will generally be sufficient. The grades of emery I use are such that the emery is deposited from water in the following times:—No. 1 settles in 1 minute, No. 2 settles in 10 minutes, No. 3 settles in between 20 minutes and 60 minutes.

The surface is polished with rouge on a pitch form. It is essential to obtain opticians' rouge, which has been well washed, and not jewellers' rouge. The proper quality of rouge I have obtained from Messrs. Cooke of York. To form the pitch surface some pitch is melted, and when thoroughly liquid is poured over the surface of a piece of plate-glass and a second piece of plate-glass, the surface of which has been thinly coated with dilute glycerine, is pressed down on the top of the pitch. Weights are placed on the upper glass till the pitch is cold, when the glass can be slid off. The polishing is continued till on examining the surface with a low-power microscope no pitting can be seen. Quite

a light pressure of the tip of the finger must be used during the polishing, which will take from 10 to 30 minutes.

To give the polished surface its reflecting coating a very thin layer of the platinizing liquid is uniformly painted over the surface with a clean brush, and the disk is placed on a metal plate over a water-bath. When the coating is quite dry the disk is heated in a small muffle made by bending a sheet of thin sheet-iron and placing it over a large Bunsen flame. The heating must be continued till a fairly bright red is attained. It is an advantage to raise the temperature of the disk to a red heat as quickly as possible, for if the heating is slow the platinizing compound tends to volatilize before it decomposes. The surface thus obtained will be very bright and will not require polishing. If the film of platinum is too thin a second coating of the platinizing liquid can be given.

In this way a mirror is obtained which, however, is about a millimetre thick. To reduce it to a more suitable thickness the platinum surface is temporarily protected with a coating of pitch or some other varnish, and the other surface of the disk is ground away on the brass surface-plate with carborundum till the desired thickness is obtained. It will be found quite easy to prepare a mirror having a diameter of one centimetre and a thickness of two-tenths of a millimetre. Such a mirror will weigh about .045 gram.

In order to support the mirror the tag is fused, by means of a small oxyhydrogen flame, to a thin rod of fused silica and the magnets are cemented to this rod.

The above method of constructing galvanometer mirrors avoids the necessity of grinding and polishing the surface of a very thin disk, an operation of great difficulty, and is only rendered possible by using a non-corrodible reflecting surface so that the light has not to traverse the quartz disk. Also the excessively small coefficient of thermal expansion of quartz enables us to obtain a disk of the material which is so free from internal strains that when we grind away one side the form of the other side is not appreciably altered. Lastly, the method of attachment of the mirror to the stem, since it avoids all cements, entirely does away with the risk of distortion due to the contraction of the cement.

Platinum surfaces prepared as above described have not quite such a large reflecting power as glass backed with silver. A comparison between a platinum surface which had been exposed quite unprotected to the air of the laboratory for a month and a silver on glass mirror made by Hilger showed that the reflecting power of the platinum was about seven-tenths of that of the silver. Any difficulty due to this smaller reflecting power can be got over by using a transparent scale with opaque lines backed by a flame, in place of the ordinary opaque scale illuminated by diffuse light.

Platinum mirrors appear as if they might be of considerable use where a metallic mirror is required, and where silver would be likely to tarnish. When glass is used considerable care has to be used, in the first place not to increase the temperature so quickly as to crack the glass, and secondly not to raise the temperature to such a height as to alter the figure of the glass by softening. When crystalline quartz is used no softening is to be feared. The temperature has, however, to be altered *very slowly* or the quartz will crack. With care, however, very perfect mirrors have been obtained on quartz.

Platinum deposited in this way forms a very good coating for producing "half-silvered" mirrors for use in interference experiments and such instruments as those recently described by Sir Howard Grubb (Sci. Trans. R. Dublin Soc. vii. p. 385, 1902). The preparation of a surface having a given reflecting power is much easier in the case of platinum than in the case of silver, and once such a surface has been obtained it seems to be practically unalterable.

#### DISCUSSION.

Mr. C. V. BOYS congratulated the author upon a valuable and interesting paper. The subject of mirrors was one which for many years had troubled and perplexed experimenters. It was surprising that a new method of making mirrors, such as that described in the paper, could have so many advantages over the usual processes.

Mr. J. W. SWAN expressed his interest in the paper, and said he was glad to see that the seed sown by Mr. Boys in



the employment of fused quartz was being cultivated to-day. The paper was a valuable practical contribution. He asked for the composition of the platinizing solution.

The CHAIRMAN, in congratulating the author, said he had had an opportunity of discussing with Dr. Watson the uses to which these mirrors might be put, and he had seen their many advantages in a vertical-force magnetograph at the National Physical Laboratory.

Dr. WATSON said he thought the composition of the solution was a secret, but it was a comparatively inexpensive liquid obtainable from Messrs. Johnson and Matthey.

*L. Direct-Vision Spectroscope of one kind of Glass.*

*By T. H. BLAKESLEY, M.A.\**

THE fundamental principle underlying the action of this instrument is the following:—Starting with the ordinary formula connecting  $\mu$  the index,  $A$  the refracting angle of a prism, and  $D$  the minimum deviation—

$$\mu \cdot \sin \frac{A}{2} = \sin \frac{A + D}{2},$$

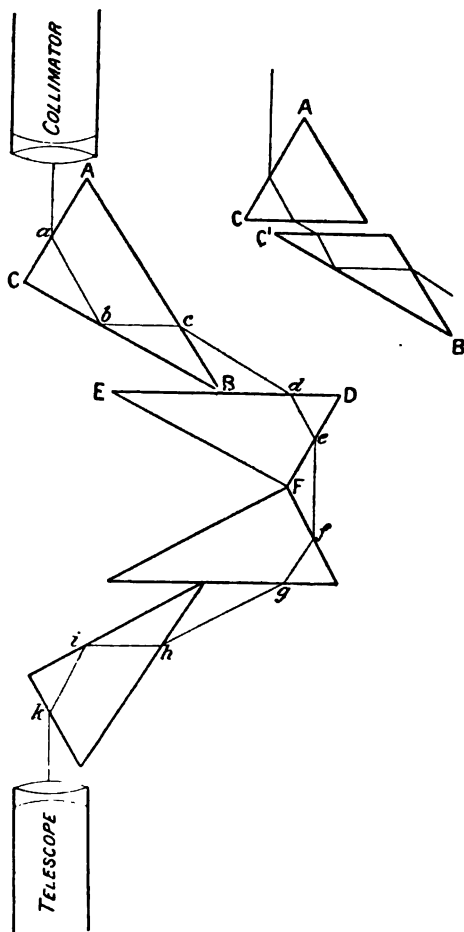
if the angle  $A$  is so chosen that the deviation shall be equal to the refracting angle, *i. e.*  $D = A$ , then

$$\mu = 2 \cos \frac{A}{2}.$$

The glass being selected, and the ray of light which is to be directly transmitted being chosen, the refracting angle must be constructed in accordance with this simple formula. Since the refracting angle is thus to be equal to the angle of minimum deviation, it is clear that the light from the collimator must be directed upon the prism at right angles to the side from which the light is to emerge, and when the light emerges the ray selected will be at right angles to the side upon which incidence took place. If then the emergent

\* Read May 8, 1903.

light is received upon an obtuse-angled isosceles prism so placed that its base is parallel to the selected ray, the whole of the light will pass through, suffering reflexion once, and emerging in the following way:—The selected ray will be



parallel to its course before incidence on the isosceles prism, and therefore still at right angles to the face on which the first incidence took place.

The rest of the rays will have changed sides as regards the selected ray, and therefore be in a condition to receive an

extra dispersion by a prism of the same refracting angle as the original one, but having its point turned so that the selected ray is brought back to parallelism with its original course.

Now the first prism and the isosceles may be and are in fact merged into one right-angled prism, as shown in the accompanying plan, where also the hypothetical condition of the separation of these two is also shown, for explanation merely, in the right-hand top corner. In the plan the course of the ray selected is shown by *a b c d e f g h i k*, and then into the telescope (p. 508).

The collimator and the two first prisms form one rigid system, the telescope and the two last prisms another, and these move relatively round the symmetric point F.

It is clear that the telescope might have been fixed so as to receive the light emerging from *e*. In that case parallelism but not collinearity would have been secured. With the four prisms both conditions are reached.

When a ray which is not the selected one is brought into the centre of the field, it is clear that though between the second and third prisms the ray is not parallel to the collimator, it is still passing symmetrically through the four prisms as a whole, and therefore with minimum deviation.

The second and third prisms in the plan have been drawn of the same shape as the first and fourth, but as one of their three sides is not, in this instrument, employed, they may be much curtailed. I have thought it proper to draw them as shown that the parallelism of the various sides, where it exists, may be strongly brought out.

In conclusion it may be stated that in the actual instrument shown the glass has been selected so as to give admirable visibility from A to H, the line F very nearly corresponds with the selected ray, and there is a dispersion of  $18^{\circ} 20'$  between A and G.

#### DISCUSSION.

Prof. S. P. THOMPSON congratulated the author upon the design of the instrument and the ingenious principle involved.

Prof. J. D. EVERETT said that in all previous direct-vision spectroscopes half the prisms increased the dispersion and other half diminished it; whereas in this instrument all the

prisms combined to increase it. He regarded the arrangement as a triumph of inventive skill.

The CHAIRMAN said he agreed with the remarks of Prof. Thompson and Prof. Everett. He had had an opportunity of examining the instrument at the National Physical Laboratory, and found the dispersion large and the definition good.

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### LI. *On the Mathematics of Bees' Cells.*

*By* Prof. J. D. EVERETT, *F.R.S.\**

FOR the literature of this subject reference may be made to a critical summary by Dr. Glaisher in the *Philosophical Magazine* for August 1873, which contains an exposure of several popular errors. Later results of observation will be found in Darwin's '*Origin of Species*,' pp. 221-227.

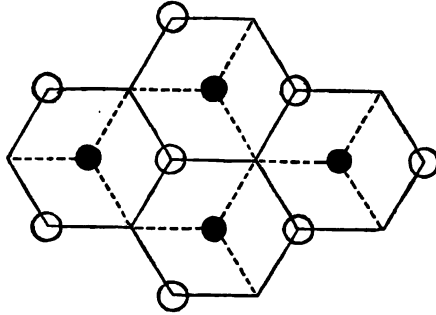
A bees' comb consists of cells combined in double layers. Each cell has the form of a regular hexagonal prism with 3 of the 6 corners at one end sliced off so as to give a pointed apex. The 3 faces which meet at the apex are rhombuses symmetrically arranged, and 3 corners of each rhombus lie upon edges of the hexagonal prism. Three alternate edges of the prism are accordingly longer than the other three, and we shall denote this difference of length by  $h$ . Then  $h$  will also denote the distance of the apex from the plane of the ends of the 3 longer edges. The length of a side of the regular hexagon which is the cross-section of the prism will be denoted by  $s$ .

Any number of equal and similar sharpened prisms, constructed according to this specification, can be fitted accurately together, in two layers, in such a way that the apex of a member of one layer is inserted between three apexes belonging to the opposite layer. The axis of each prism will then be in line, not with an axis, but with the common edge, of 3 prisms belonging to the other layer.

The annexed diagram is specially designed to set forth the relations of the parts in the clearest manner by projecting them on a plane perpendicular to the axes of the prisms.

\* Read May 8, 1903.

The ends of the longer edges of both sets of prisms lie in the same plane, which is the plane of the paper. The two



sets of apexes are represented by the two symbols ● and ○, and lie at equal distances  $h$  from the plane of the paper on opposite sides of it. All points of meeting not so marked lie in the plane of the paper. Two sets of hexagons are indicated, one by continuous and the other by dotted lines. They are the projections of the two sets of prisms. The rhombuses into which the figure is divided are projections of the rhombuses which meet at the several apexes; each rhombus-edge being in the plane of one of the prism-faces. The plane of one set of apexes is at a distance  $2h$  from the plane of the other set.

The projected length of a rhombus-edge is  $s$ , and its actual length  $\sqrt{(s^2 + h^2)}$ .

The long diagonal of a rhombus lies in the plane of the paper, and is  $s\sqrt{3}$ ; the shorter diagonal is  $\sqrt{(s^2 + 4h^2)}$ . If  $\theta$  denote an acute angle of a rhombus we have

$$\cos \frac{1}{2}\theta = \frac{\sqrt{3}}{2} \frac{s}{\sqrt{(s^2 + h^2)}},$$

whence

$$\cos \theta = \frac{s^2 - 2h^2}{2(s^2 + h^2)}.$$

If  $\phi$  denote the acute angle which a prism-edge makes with the rhombus-edge that it meets, we have

$$\cos \phi = \frac{h}{\sqrt{(s^2 + h^2)}}.$$

Changes in the value of  $h$  will not affect the volume of a cell, but they will affect the quantity of wax required for building the cell. If  $h$  were zero the prism-edges would all terminate in the plane of the paper, which would also contain the rhombuses. As compared with this standard of reference, the area of a prism-face is less by  $\frac{1}{2}sh$ , and the area of a rhombus is greater by  $\frac{1}{2}s\sqrt{3}\sqrt{(s^2+4h^2)} - \frac{1}{2}s^2\sqrt{3}$ . To give proper weights to these two items on opposite sides of the account, we must know the ratio of the number of prism-walls to the number of rhombuses. Each cell has twice as many prism-sides as rhombuses; and in the comb, except at the outside, each rhombus, as well as each prism-wall, is common to two cells. At the outside, the walls exposed also comprise twice as many prism-walls as rhombuses. We must therefore reckon two prism-faces to one rhombus, and the net saving in area is

$$sh - \frac{1}{2}s\sqrt{3}\{\sqrt{(s^2+4h^2)} - s\},$$

Omitting a constant term and a constant factor, the quantity to be made a maximum is

$$h - \frac{\sqrt{3}}{2}\sqrt{(s^2+4h^2)},$$

provided that the rhombuses have the same thickness as the prism-walls. If they are  $n$  times as thick as the walls, the quantity to be made a maximum is

$$u = h - n\frac{\sqrt{3}}{2}\sqrt{(s^2+4h^2)};$$

whence, putting  $\frac{du}{dh} = 0$ , we find  $s^2 = (12n^2 - 4)h^2$ ,

or

$$\frac{s^2}{12n^2 - 4} = \frac{h^2}{1} = \frac{s^2 + h^2}{12n^2 - 3} = \frac{s^2 - 2h^2}{12n^2 - 6},$$

giving

$$\cos \theta = \frac{2n^2 - 1}{4n^2 - 1}, \quad \cos \phi = \sqrt{\frac{1}{3(4n^2 - 1)}}.$$

The usual calculation assumes  $n = 1$ , giving

$$\cos \theta = \frac{1}{3}, \quad \cos \phi = \frac{1}{3}.$$

The trihedral angles, of which there is one at each apex, and one at the end of each of the shorter prism-edges, are each composed of 3 plane angles whose cosine is  $-\frac{1}{3}$ , the inclinations of their planes being  $120^\circ$ . The form thus deduced is regarded as the normal form of bees' cells.

It is closely related to the most compact system of piling of equal spheres. In this system each sphere touches 3 spheres in the layer below, 3 in the layer above, and 6 in its own layer. If we omit the 3 upper or the 3 lower, the tangent planes at the 9 remaining points of contact represent the 9 walls which bound a cell.

Again, the 9 walls (including 3 pairs of parallel walls) are perpendicular to the 6 edges of a regular tetrahedron; and the 12 lines of junction of these walls (including 3 pairs of parallels and 1 set of 6 parallels) are perpendicular to the 4 faces of the same tetrahedron.

According to observations cited by Darwin, the actual value of  $n$  averages about  $\frac{3}{2}$ . This gives

$$\cos \theta = \frac{7}{16}, \quad \cos \phi = \sqrt{\frac{1}{24}},$$

for minimum consumption of material.

#### DISCUSSION.

Prof. S. P. THOMPSON said that he could not agree with the author that the bees for a given volume of cell wanted to use a minimum of material. He thought the amount of wax necessary was determined by other considerations.

Prof. EVERETT said he thought the bees were guided by simplicity of construction. If we suppose the bees in the two layers of cells to be arranged like two tiers of cannon balls in the most compact piling, the centres of the bees coinciding with the centres of the balls, each bee takes part in the building of walls between itself and its nearest neighbours, each wall being midway between the two bees, and at right angles to the line joining them. According to the best authorities, there was much irregularity in the construction of bees' cells, but the received form (described in the paper) was a fair average.

LII. *Exhibition of Nernst Lamps, showing their Development from the Experimental Form up to the most recent types.* By Mr. J. STÖTTNER.\*

MR. STÖTTNER commenced by giving a short account of the history of the Nernst lamp, and explained briefly the principle of its action. The oxides used for the glowers are thoria, zirconia, and other rare earths thereto related, such as oxides of yttrium and cerium. A paste of these is formed, and small rods or tubes are pressed through a suitable nozzle. These are hardened and cut into small lengths, and practically the principal part of the lamp is finished. Several of these rods were passed round for the inspection of Fellows. The chief difficulty in the practical lamp is in the design of a durable automatic heater to heat the filament up to conducting point. A number of automatic arrangements which have been designed for disconnecting the heater were shown. Another important part of a Nernst lamp is the bolstering resistance, which in its final development consists of a thin iron wire sealed in a glass bulb filled with hydrogen gas. If a lamp is used without a bolstering resistance, as soon as a certain critical potential is reached the current increases, at first slowly and then quicker and quicker, the potential remaining constant, until the lamp burns itself out. This phenomenon was shown experimentally. Various forms of lamp were exhibited. One with two glowers and one heater overcomes the difficulty of thick glowers. A projection lamp was shown with three glowers in parallel requiring 300 watts. The glowers in this case were heated artificially. Mr. Stöttner also exhibited and described a pole-finder for use with lamps using direct current.

DISCUSSION.

The CHAIRMAN said he would like to see details of the life and economy of these lamps under various conditions. The lamp was in its infancy, and probably even more satisfactory lamps would be forthcoming.

\* Read May 22, 1903.



LIII. *The Electrical Resonance of Metal Particles for Light-Waves. Third Communication.* By R. W. WOOD, *Professor of Experimental Physics, Johns Hopkins University.*

SINCE the appearance of the two preceding papers (Phil. Mag. vols. iii. & iv., 1902; Proc. Physical Soc. *antea*, pp. 166, 276) on the above subject I have made further investigations, which appear to confirm the provisional hypothesis of electrical resonance, which was adopted to explain the very brilliant colours of films made up of metal granules of the order of magnitude of light-waves.

I have succeeded in obtaining the coloured films in prismatic form, and have established the fact that they exhibit anomalous dispersion for waves longer and shorter than the ones which are refused transmission. This was observed for electrical waves passing through a prism built up of tinfoil resonators by Garbasso and Aschkinass. I have obtained the coloured films on the walls of a tube in which I had fused a quantity of magnalium alloy *in vacuo*. The film was permanent in air, but the colours vanished as soon as the film was moistened with a little very dilute acid, owing to the conversion of the metal granules into a salt. I have also obtained coloured films by the cathode discharge from an electrode of selenium, though the colours in this case were not nearly as brilliant as those obtained by the distillation of the alkali metals. The microscope showed these films to be granular, and experiments with the quartz spectrograph demonstrated that they were very transparent to ultra-violet light, for which homogeneous films of selenium of the same thickness are absolutely opaque.

The silver films, red, purple, and blue, which I described in my second paper, seemed most suitable for continuing the experiments, owing to the comparative ease with which they are prepared and their permanency in air. On attempting to repeat the experiment, I was somewhat annoyed to find that the silver solution dried on the plates with no trace of colour, a thin deposit of a black powder being the only result. This powder, if rubbed with the finger,

gave a blood-red streak on the plate, which resembled in every respect the coloured deposits obtained last year. I tried cleaning the glass more carefully, using fresh chemicals and distilled water ; but all to no purpose. It finally occurred to me, however, that I had formed the original deposits on some old lantern-slide plates, from which the gelatine had been removed with hot water. Possible a film of gelatine of infinitesimal thickness might have been the necessary factor. To test this I wetted a sheet of glass and rubbed it over with a small thread of Nelson's photographic gelatine. The plate being cold, only the slightest trace of gelatine could have dissolved in the film of water. The plate was then drained off and dried on a hot metal plate. On flowing this plate with the silver solution and drying it rapidly as before, I obtained a most wonderful film, as red as the densest ruby-glass over most of its extent, but with several patches of deep blue-violet, as rich in colour as dense cobalt-glass. The presence of the gelatine seems in some way to keep the small particles from collecting into aggregates (the black powder). It will be remembered that in my first paper I alluded to an experiment in which the cooling of a bulb, and the condensation of the hydrocarbon vapour on the coloured film, sometimes destroyed the colour permanently, the minute sodium particles collecting into larger aggregates, which diffracted the light, and showed the pearly lustre, but exhibited no trace of colour by transmitted light.

As the formation of these films makes a most brilliant lantern experiment, I will give more explicit directions for their preparation. The solution is one described by Carey Lea. Three solutions are prepared ; a 30-per-cent. one of ferrous sulphate, a 40-per-cent. one of sodium citrate, and a 10-per-cent. one of silver nitrate. Fourteen c.cms. of the citrate solution are mixed with 10 c.cms. of the ferrous sulphate solution, to which is then added 10 c.cms. of the silver nitrate solution. A dense black precipitate at once forms, and the whole is at once poured into a filter. As soon as the liquid has entirely run through, the precipitate is washed with 10 cms. (*not more*) of distilled water. This is to remove the salts which make the precipitate insoluble. After the water has entirely passed through the filter, about 25 c.cms.

of distilled water are poured into the filter, and the blood-red solution which runs through collected. As it does not keep very well, it is best to prepare it on the day on which it is to be used.

A sheet of glass is washed clean, rinsed with fresh water, and the wet surface rubbed over with some shreads of gelatine. It is then drained for a few seconds and dried on a hot plate. A little of the silver solution is flowed over it, the surplus being drained off. If too much gelatine has been used, precipitation is apt to take place, the deposit taking the form of floating shreads of a reddish membrane. If no considerable precipitation occurs, the plate, which should have been quite warm when flowed, is placed once more on the hot plate until dry. The films formed in this way are usually deep red in colour, though sometimes patches of deep violet form, with sharply defined edges. As one may make a dozen trials without obtaining the violet patches, I endeavoured to find some way of producing them at will; and finally hit upon the right expedient. When the plate is about half dry, with a steaming film and a few small pools of the hot solution, it is removed from the hot plate, held at an angle, and treated with a few drops of alcohol, which are allowed to run down across the still damp portion of the plate. These portions speedily dry into a most gorgeous mosaic of red, purple, and violet patches, the experiment being especially striking in the lantern, as it occupies but a few seconds, and the colour-display spreads over the plate like the blaze of a sunset. So far as I have been able to find, these brilliantly coloured films were never obtained by Carey Lea, though the solution used is one that he employed in his experiments on allotropic silver.

Any desired depth of colour can be obtained with these films by merely allowing more or less of the solution to remain on the plate. I have films of such a deep red that they are almost opaque, a gas-flame being barely visible through them. The light which does get through is regularly transmitted, that is, the films are not turbid media. The spectroscope shows that the absorption-band is wider and less sharply defined than is the case with some of the purple potassium films, which have a rather narrow and very black band in the yellowish green. This can be explained by

assuming that there is not a great regularity in the size of the particles, and consequently less sharp selective resonance. Inasmuch as some of the sodium films had a bright apple-green colour, in other words absorbed both the red and blue, it seemed worth while to see whether the silver films exhibited the same phenomenon. Red and violet films were formed on a quartz plate, and the absorption-spectra photographed with a quartz spectrograph. It was found that they were transparent to the whole ultra-violet region, even the last two faint cadmium lines which almost all media cut off, appearing on the plate. If a second band is present it must be located in the infra-red region.

Before continuing the experiments with these highly coloured silver films, it seemed best to establish beyond any doubt that they were analogous in every respect to the films obtained with the alkali metals. One respect in which they differ is the absence of much effect when they are moistened with ligroin. It will be remembered that the films formed by distillation in exhausted bulbs showed most remarkable colour-changes when the hydrocarbon vapour was caused to condense on the wall by the local application of cold. This difference is not of serious moment ; for it is quite possible that the silver particles are already immersed in some medium (possibly gelatine) which prevents the ligroin from entering. As I have mentioned in my previous paper, a very slight change of colour is produced by the ligroin ; but only close examination makes it evident. The red films of silver can be changed to purple and blue by the local application of heat. This was also true of the alkali metal films. I mentioned in my first communication that where the sodium deposits were very scant the particles scattered a bright green light, the appearance being somewhat as if the inside of the bulb had been washed over with a solution of fluoresceine. This light was of the wave-lengths of the light absorbed where the film was thicker. Only films too thin to show any colour by transmitted light exhibited this phenomenon. For convenience I spoke of this light as the "fluorescent light," without intending to convey the idea that it has any real connexion with fluorescence.

It remained only to be seen whether silver deposits could be obtained which showed this peculiarity. A plate was flowed with the silver solution, and then partly rinsed off with distilled water and dried.

By transmitted light there were traces of colour in patches, though most of the plate appeared colourless. On holding it in a beam of strong sunlight in a dark room there appeared many patches which exhibited a bottle-green diffused light, not quite as bright and pure as that shown by sodium, but in every way analogous to it.

Inasmuch as all of the peculiarities shown by the films of the alkali metals have been observed to a greater or less degree with the silver films, it seems safe to conclude that the cause of the colour is the same in the two cases.

An attempt was now made to determine whether the films show anomalous dispersion as we should expect them to do if the colour is due to resonance.

A sheet of thin plate-glass was prepared with gelatine and flowed with the silver solution. A number of glass tubes were then laid side by side on the plate, the fluid being drawn up by capillarity into prisms. The plate was then warmed until the prismatic strips of fluid had dried, when the glass tubes were removed. On examining the plate it was found that some very perfect prisms had formed, which resembled closely the cyanine prisms which I have described in a previous paper. The portion of the plate which seemed to carry the most perfect prism was cut from the glass sheet and mounted on the table of the spectrometer, a small portion of the glass having been previously cleaned to enable a reading to be taken of the undeviated image of the slit. The prism was screened with black paper to cut off the light which did not pass through the most perfect portion, and the slit of the instrument illuminated with light from a monochromatic illuminator. By alternately exposing the clear glass and the prism, readings of the deviated and undeviated images could be taken. It was found that when blue-violet light was employed the prism did not deviate the image by any measurable amount, while with red light the deviation amounted to several times the width of the image of the slit.

The latter was considerably broadened by diffraction, as is always the case with strongly absorbing prisms.

The prism was of a deep red colour, but transmitted violet freely, the absorption-band being in the green. It was found that the deviation was less for the extreme red of the spectrum than for the orange-red, which is just what we should expect. The absence of any deviation in the case of the violet light means of course that the refractive index does not differ much from unity for these waves. To determine the index for the red it is necessary to know the angle of the prism. This was determined by observing the images of the slit reflected from the strip of clear glass and the surface of the prism, the required angle being one-half of the observed angle. This angle was found to be  $1^{\circ} 15''$ , while the deviation for red light was  $2^{\circ} 42''$ . The refractive index calculated from these observations turns out to be 3.15, or about that of selenium for yellow light.

This is practically proof positive that the cause of colour is resonance, though the question is still open as to whether it is resonance of small metal particles in a manner analogous to the action of the tinfoil resonators on electro-magnetic waves, or a resonance within the molecule, as in the case of the aniline dyes. Though I have not yet devised any crucial experiment which enables me to distinguish between the two, I have observed differences in the behaviour of these metal films from that of films formed of dye-stuffs, which makes it seem extremely probable that the action is different in the two cases.

To these arguments may be added the one that it seems unlikely that so many different metals should exhibit such similar molecular absorption, and that the granular condition should be essential to the production of colour, for I have succeeded in detecting the granules in every case by means of the microscope.

Let us now consider some of the differences between the action on light of these coloured films and films formed of aniline dyes. A film of granular silver can be formed which resembles very closely a film of cyanine, both having absorption-bands in the middle of the visible spectrum. If a very

thin film of silver is prepared which exhibits a light purple colour by transmitted light, the colour is much less marked, *i. e.* the absorption is less, when the plate is held at an angle of say 30 degrees with the incident light than it is at normal incidence. Moreover, the colour changes from purple to red, the absorption-band appearing to move down the spectrum a trifle. Possibly a simple broadening of the band would produce this same colour change owing to the greater sensitiveness of the eye for red. A cyanine film does not exhibit this peculiarity, the colour of the transmitted light remaining nearly constant for varying angles of incidence.

The change in depth and hue of the colour when the incidence is made oblique is probably due to the fact that the absorption is different when the incident light has a component of the electric vector perpendicular to the surface, which, of course, is not the case when the incidence is normal. If the light is polarized to start with, this is found to be the case, the colour of the transmitted light being bluish-purple when the electric vector is perpendicular to the plane of incidence, and red when it is parallel to this plane in which case there is a component normal to the surface. These changes are not obtained with the film of cyanine. In the course of a recent discussion of the problem which I have had with Professor J. J. Thomson, he expressed the opinion that the capacity of a sheet of resonators would be greater, and the period of vibration consequently longer, when the electric vector was parallel to the sheet. This is in agreement with the observations which I have made with the silver films, the absorption-band moving towards the red when the plane of polarization is so oriented that the electric vector has no component normal to the surface.

With sodium and potassium films I have obtained just the opposite effect, the absorption-band moving in the other direction. These results appeared at first to be very confusing, until I finally discovered what I believe to be the explanation.

I have studied the behaviour of the films at oblique incidence with polarized light with considerable care, and have obtained results which appear to be concordant among themselves.

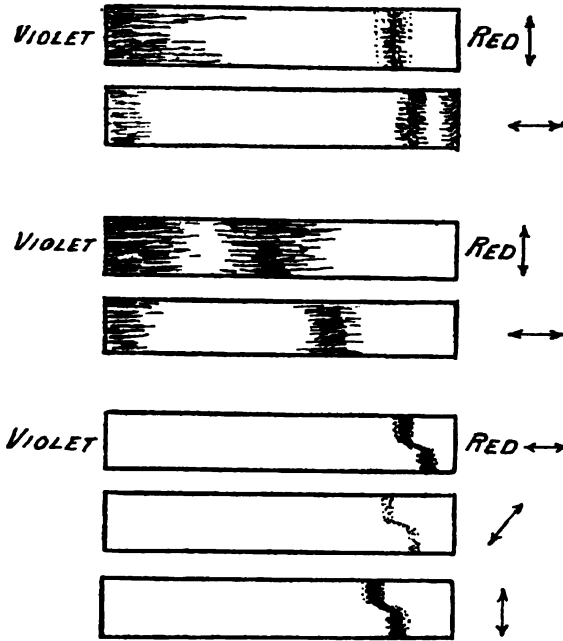
If the plane of incidence is horizontal and the electric vector is parallel to this plane, *i. e.* with a component perpendicular to the surface, we find for example a heavy absorption-band in the green. As the plane of polarization is rotated through a right angle the band in some cases shifts its position in the spectrum (sometimes in one direction and sometimes in the other) and sometimes simply fades away entirely without undergoing any shift. On examining the spectrum with greater care, however, I found that in general other bands are present. If the band in the green moves towards the red, a band comes into the spectrum from the red end to meet it, and another band which was originally in the violet moves out of the spectrum in the direction of the ultra-violet. It is difficult to say at present whether the appearance and disappearance of these two fainter bands is due to their motion along the spectrum, or to the fact that one fades away and the other springs into existence, as in the case above cited. This difficulty is due to the fact that a part of the band lies outside of the visible spectrum, and a fading away can easily be mistaken for a drift. I am of the opinion that in some cases we are dealing with one phenomenon, and in other cases with the other.

I have examined several films in which a band in the yellow and one in the blue distinctly approached each other when the plane of polarization was rotated through a right angle. This explains why it is that a single band near the centre of the spectrum is sometimes seen to move in one direction and sometimes in the other.

In the one case it was doubtless the right-hand band of a pair which approached (the other lying in the invisible portion of the spectrum), in the other case it was the left-hand band of an approaching pair. Some typical cases of the changes which occur when the plane of polarization is rotated are shown in the diagram. The plane of incidence is horizontal in every case, *i. e.* the sheet of resonators stands vertical, and at an angle of about 45 degrees with the incident light. The direction of the electric vector is indicated by the double arrow. In general the band drifts without much change in intensity, though in some cases it fades away almost to the



vanishing point when the plane of polarization is at 45 degrees to the plane of incidence. A case of this kind is shown in



the last three spectra of the figure. The band in this case was crooked, as the slit of the spectroscope was placed at a point where the colour of the film changed quite abruptly from blue to purple.

The appearance of several bands in the spectrum suggests that we are dealing with something of the nature of multiple resonance, and it is to be hoped that some of the mathematical physicists will work out the behaviour of a sheet of small spherical resonators at normal and oblique incidence for vibrations polarized in different planes.

LIV. *On the Positive Ionization produced by Hot Platinum in Air at Low Pressures.* By O. W. RICHARDSON, B.A., B.Sc., Fellow of Trinity College, Cambridge\*.

[Plate IX.]

THE experiments to be described were originally undertaken in order to examine the connexion between the leak from a hot wire, when charged positively and surrounded by air, at a low pressure, and the potential and temperature of the wire respectively.

The arrangement of apparatus at first used was similar to that employed by the author in investigating the negative leak from hot conductors†. The wire, which was in the form of a spiral, was supported along the axis of a cylindrical electrode from which it was insulated. The spiral was of pure platinum wire .1 mm. thick, and was heated by an electric current, its temperature being determined by means of its resistance. It was found that the absolute temperature could easily be kept constant to one part in a thousand, so that it did not vary more than one degree at the highest temperature investigated. The vacuum-tube containing the spiral and electrode was connected with a Töpler pump and McLeod gauge, so that the gas could be kept at any desired pressure.

The leak was measured by means of a quadrant electrometer. The wire was charged to any desired positive potential, whilst the surrounding cylindrical electrode was connected to one of the quadrants of the electrometer, the other being earthed. In general the experiments were made at such a temperature that the currents could conveniently be measured without adding any external capacity to that of the electrometer. The temperature was always below that at which the negative leak became detectable.

The first experiments were made to determine the way in which the current from the wire varied with the applied potential, the other conditions being maintained constant.

\* Read June 12, 1903.

† Proc. Camb. Phil. Soc. xi. p. 286; Proc. Roy. Soc. lxxi. p. 415.

The temperature was  $442^{\circ}\text{C}$ . The pressure remained constant, and equal to  $\cdot 00625$  mm. of mercury. Observations were taken first with no potential on the wire, and then for every additional 40 volts up to 400; the values of the current\*, in scale-divisions per minute, obtained in this manner are marked thus, x, on the accompanying diagram (Pl. IX. fig. 1). The observations were then repeated, the potential being continuously decreased by 40 volts down to zero; the values obtained in this way with decreasing potential-differences are marked thus, o.

It will be seen that the ascending observations give rise to a curve which is slightly convex to the axis of current; on the other hand, the curve which represents the descending observations possesses about an equal curvature, but is concave to the current-axis. The disparity of the two series of observations is due to the falling-off of the current from the wire with time, a point which is examined in detail later. It will be seen that the time-effect can be allowed for by taking the mean of the two observations belonging to the same potential, since this would be—approximately at any rate—the current for that potential at a time half-way between the two experiments. This time is the same for every two observations, and is identical with that at which the reading for 400 volts was taken. This reasoning assumes that every observation takes the same length of time, a condition which was approximately fulfilled.

It will be seen that the current-E.M.F. curve is almost a straight line passing through the origin, so that the current is nearly proportional to the electromotive force. A repetition of the observations gave the same approximately linear relation, and showed that the fact that the mean point for 40 volts fell off the curve was due to accident, for it did not occur again.

Some experiments on the relation between the current and the E.M.F. were also made in hydrogen at a pressure of  $\cdot 6$  mm. In this case the apparatus was slightly different, the spiral being parallel to, and about 1.5 cm. distant from, a flat circular electrode to which the leak was measured. The

\* Throughout this paper 1 scale-division is equal to  $\cdot 02$  electrostatic units of quantity.

temperature was  $692^{\circ}\text{C}$ . The relation between the current in scale-divisions per half minute and the potential-difference in volts is given in the following table :—

Voltage.	Current.
40	550
80	1300
120	2600
160	3650
200	5150

It will be seen that the relation between current and P.D. here is not linear, but that the current increases more rapidly than the voltage with high voltages.

Further experiments were next made with the object of testing the explanation of the discrepancy between the ascending and descending curves shown in fig. 1. With this aim the way in which the current under a constant voltage varied with time was observed. The temperature was maintained at  $467^{\circ}\text{C}$ .; the pressure being  $\cdot 00625$  mm. Throughout the observations a potential of  $+40$  volts relative to the cylindrical electrode was maintained on the wire. As in the previous experiments, there was no leak when the wire was put to earth or when it was charged negatively.

Corresponding values of the current in scale-divisions per minute, and of the time in minutes from the commencement of the experiments, have been plotted on squared paper (Pl. IX. fig. 2). It will be seen that the observational points fall very approximately on the curved line shown. The form of the curve shows that the rate of decay of the current is great at first, but after about an hour almost vanishes. The leak then becomes constant, and approximately equal to 13 scale-divisions per minute. For brevity we shall call the final value of the current the "steady leak"; the difference between the value of the current at any time and the steady leak may be called the "induced" leak. The propriety of using the term induced in this connexion will be demonstrated later.

We can explain these results if we suppose the induced

leak to be due to some substance which gradually decomposes under the influence of heat into at least one positive ion and possibly other products. The reaction is supposed to be monomolecular, and may be represented by the equation



where  $X$  represents the unknown substance,  $n$  is the number of positive ions formed from each molecule of  $X$ , and  $Y$  represents the other products if they exist.

The laws of chemical dynamics then give at once

$$-\frac{dX}{dt} = kX,$$

where  $k$  is the velocity of the reaction ; so that

$$X = A_1 e^{-kt}.$$

But if the induced leak be denoted by  $y$ ,

$$y = n \frac{dI}{dt} = -\frac{dX}{dt} = kX = kA_1 e^{-kt} = Ae^{-kt},$$

so that

$$\log y = B - kt.$$

( $A_1$ ,  $A$ , and  $B$  are different constants.) Evidently on this view, if we plot the logarithm of the difference between the actual current and the steady leak with the time, a straight line ought to be obtained.

The observations have been reduced in this way in fig. 3, and it will be seen that all the points fall very nearly on the straight line drawn. The irregularities are due to the fact that the wire could not be treated in exactly the same way between each two observations, and it is probable that the rate of decay depends not only on the time which has elapsed, but also on some other circumstances.

A series of experiments was now made with a new tube in which all the metal parts were of platinum, so that the whole could be carefully cleaned out by boiling in nitric acid and washing with distilled water. After this treatment, it was found that the wire gave quite as considerable a leak as one which had not been cleaned, so that the positive ionization is not due to superficial impurities soluble in nitric acid.

With this wire an attempt was made to see if the rate of decay of the variable leak depended on the temperature to

which the wire was heated. The method used was to maintain the wire at a constant temperature, and take readings of the current every eight minutes. The wire was then heated to a somewhat higher temperature and the process repeated. The following table gives the results in the order in which the experiments were made. Owing to the magnitude of the

Temperature $\theta$ .	Time wire at $\theta$ .	Actual Time.		Current.
		Hours.	Minutes.	
515° C.	0	1	37	15,000
	8	1	45	12,000
	16	1	53	7,000
	24	2	1	4,000
577° C.	0	2	20	31,000
	8	2	28	36,500
	16	2	36	31,000
	24	2	44	15,500
632° C.	0	3	2	280,000
	8	3	10	58,000
	16	3	18	28,000
697° C.	0	3	24	250,000
	8	3	32	64,500
751° C.	0	3	36	360,000
	8	3	44	68,500
809° C.	0	3	48	250,000
	8	3	56	58,500
	16	4	4	23,000
751° C.	0	4	8	5,000
	8	4	16	5,500
697° C.	0	4	20	950
	36	4	56	725
632° C.	0	5	1	100
577° C.	0	5	6	46
515° C.	0	5	10	41
	4	5	14	41

leaks capacities up to 1 microfarad had to be connected to the quadrants of the electrometer to which the leak was measured. The lengths of time during which the wire had been maintained at the temperature stated are given as well

as the actual time at which the observations were taken ; the currents are in scale-divisions per half minute. During the time which elapsed between any set of readings at a given temperature and the next at a higher temperature, the temperature of the wire was intermediate between the two considered.

These results seem to indicate at first sight that at temperatures greater than  $600^{\circ}\text{C}$ . the rate of decay of the variable leak is almost constant and considerably greater than at temperatures lower than this. The conditions at each temperature are not exactly comparable, so that this result cannot be regarded as satisfactorily established. The author hopes to make further experiments on this point in the near future.

The results do, however, clearly show not only that the leak at a given temperature is much smaller if the wire has previously been heated to a higher temperature, but also that the rate of decay is much less than before. For instance, on first heating the wire to  $751^{\circ}\text{C}$ . it gave a leak of 360,000 divs. per half minute, which fell to 68,500 in 8 minutes ; whereas after heating for about 20 minutes to  $809^{\circ}\text{C}$ . the leak at  $751^{\circ}\text{C}$ . had become 5000 divs. per half minute, and suffered no appreciable diminution on heating for 8 minutes longer at the same temperature.

It is evident from these experiments that to get rid of the part of the leak which dies away rapidly, it is only necessary to heat the wire for some time at a temperature somewhat higher than that at which it is to be used subsequently. It was found, however, that the steady leak thus obtained also generally died away in time, only much more slowly ; so that the distinction, at low temperatures and pressures at any rate, is one of degree rather than kind. The complexity of the phenomena generally, and especially of the rate of decay of the leak, seem to indicate that there are several distinct substances present in the metal which are capable of giving rise to positive ions.

The fact that the positive ionization from hot wires behaves as if it were due to some substance evaporating from the wire led the author to examine whether a negative

electrode which had been kept near a hot wire charged positively became radioactive. The hot wire was maintained at a temperature of about 737 degrees centigrade for one hour, and was charged to +200 volts, the cylindrical electrode being earthed. The pressure of the gas remained constant and =.05 mm. During the whole of this time there was a steady current from the positive wire to the cylinder; so that it was thought that if the substance which disappeared from the hot wire were of the nature of an emanation it would be collected on the negatively-charged cylinder.

At the end of an hour the heating of the wire was discontinued and air was let into the apparatus. Experiments were then made to see if there was any leak from the cylinder to the cold wire. The results were purely negative; the current was at any rate less than  $1/500$  of an electrostatic unit. The experiments therefore lead to the conclusion that a negative electrode does not become radioactive by receiving the positive discharge from hot platinum.

Further experiments showed that at low enough pressures, even at a red heat, the positive leak could be completely stopped by heating the wire continuously. It is therefore quite evident that the positive leak at low pressures cannot be regarded as a definite function of the temperature of the wire. At pressures of 1 mm. or higher, however, results were obtained which indicated that there was a leak due to the surrounding gas which increased with the temperature and pressure and did not fall away with time.

The fact that the positive leak decreased with time and vanished at low enough pressures led to the view that it was due to some foreign matter present in the wire, and that this gave rise to positive ions which were carried away by the current. On this view the positive ions would probably be carried to the negative electrode and condense there. If this were so the negative electrode would acquire the power, which the hot wire lost, of discharging positive electricity when heated. A new apparatus was therefore constructed in order to test this point.



*Experiments with Two Hot Wires.*

The new arrangement (Pl. IX. fig. 4) consisted of two spiral electrodes (AB, CD) of fine platinum wire placed parallel to one another and about a centimetre apart. They were supported on copper rods ( $AA_1$  &c.) which were carefully insulated with sealing-wax. By maintaining a suitable difference of potential across  $A_1 B_1$  and  $C_1 D_1$  the spirals could be kept at any desired temperature.  $A_1$  was also connected to a battery so that its potential could be raised to  $\pm 400$  volts, whilst  $C_1 D_1$  was connected to one quadrant of the electrometer, the other being earthed. The various sealing-wax joints are indicated by shading in the diagram. All the connexions of the electrometer were carefully protected from electrostatic induction by earthed conductors.

The method of experimenting consisted in heating spiral 1 until it gave no sensible leak with  $+200$  volts at a given temperature  $\theta$ . The heating current in spiral 1 was then stopped whilst spiral 2 was maintained at a high temperature for a definite interval of time. During this time spiral 2 was, of course, earthed whilst spiral 1 was kept at  $-200$  volts. The current in the second spiral was then stopped, and after a short interval the temperature of the first spiral was raised to  $\theta$  again, and the leak with  $+200$  volts on the first spiral again measured. It may be permissible to state in anticipation that in general this procedure was found to restore to the first spiral the power it originally possessed of discharging positive electrification when raised to the temperature  $\theta$ .

The first experiments were made at pressures of about  $\cdot 001$  mm. At pressures so low as this the temperature of a wire heated by a current depends only on the strength of the current, and is independent of the pressure of the gas. In order therefore to make sure of having the wire at a constant temperature it was only necessary to observe the current through it and not to measure its resistance.

In a series of observations made on July 29th the heating current was kept constant and  $= 241$  ampere. The following values for the current were obtained at the times indicated. The current is in scale-divisions of the electrometer per minute. The pressures are also given (in mms.).

Current.	Time.		Pressure.
	hours.	minutes.	
46	12	34	·0008
43	12	40	·0008
30	12	47	·0012
22	12	59	·0009
21	1	7	·0008
17	1	15	·0009
16	1	23	·0005
15	1	31	·0008
13	1	40	·0007

The apparatus was now left till next day to see if the leaking power of the wire would be revived. The following observations were taken :—

Current.	Time.		Pressure.
	hours.	minutes.	
12	11	36	·0005
5	11	41	·0005
0	11	50	·0008
1	11	58	·0008
4	12	49	·0005

It is evident from these numbers that the wire is not revived to any great extent by being left exposed to air at a pressure of ·001 mm.

The wire was now allowed to cool and charged to —200 volts, whilst the second wire, which was earthed, was kept at a red heat for 15 minutes. On allowing everything to cool and stand for a short time, and again heating the first wire with ·241 ampere, the following values of the current were obtained with +200 volts (the units of current are the same as before) :—

Current (+ leak).	Heating current (amps.).
2250	·241
2810	·241
91	·224
136	·237

The activity induced by the second hot wire is in this case enormous compared with the greatest current (46) due to the activity which the hot wire originally possessed.

The above readings for the current were taken at intervals of about 6 minutes, so that it is evident that the value of the induced positive leak falls off very rapidly with the time when the wire is heated. In other words the induced activity is almost all driven off in about half-an-hour, and in some cases even less.

This effect is not due to ions which remain suspended inside the bulb, or to any effect produced on the walls of the tube by heating, for absolutely no leak was obtained when the first wire was cold. It is also evident from the above experiments, and from others which will be described later, that the effect persists for a considerable length of time.

Each time the experiments were repeated the induced activity was found to become continuously smaller and higher temperatures had to be employed to show the effect. This is probably due to the substance which causes the effect becoming diffused onto the walls of the tube and the cold parts of the electrodes, since it goes hand in hand with a falling off in the conductivity produced when the first wire alone is heated to still higher temperatures.

Three experiments were now made to see if the effect could be produced by merely charging up the first wire to a suitable potential, the second being cold and put to earth. The wire was charged to +200, 0, and -200 volts respectively and left for 40 minutes each time; but the conductivity was again found to be zero on heating to the original temperature. In another case the first wire was maintained at +200 volts while the second was heated for 5 minutes, and it was found that the induced activity, though definite, was smaller than when the first wire had been charged negatively.

Measurements were now made to compare the activity induced in these two cases, *i. e.*, when the first wire was positive and when it was negative with regard to the second, which was heated. In order that any two experiments may give results which are quantitatively comparable it is

necessary that the state of the second (hot) wire should remain the same throughout the experiments. To ensure this the second wire was only heated for 120 seconds each time. An experiment was first made with the first wire at  $-200$  volts, then with the wire at  $+200$  volts, and so on. The fact that the activity induced in the first and third experiments (with the first wire negative) was approximately the same shows that the state of the second wire had not greatly altered. The induced activity here was small in all cases owing to the short time during which the second wire was heated.

The following table gives the actual numbers which were obtained. The current which was used to heat the first wire was  $\cdot 286$  ampere ; in all cases this current produced no leak before the second wire was treated in the manner described above. In each case in measuring the leak  $+200$  volts was put on the first wire. The pressure was  $\cdot 001$  mm.

Potential of First Wire when Second Heated.	Activity Induced in First Wire.
$+200$ volts.	5
$-200$ „	26
$+200$ „	11
$-200$ „	20

These results lead to the conclusion that the activity induced when the first wire is negative is about three times as great as when the first wire is positive. A second series of experiments, which are more satisfactory in so far as they were taken when the second wire was in a more active state, and the effect observed was therefore much greater compared with incidental uncertainties, show that the disparity between the two cases is still greater. In this case the pressure was  $\cdot 067$  mm. One observation was taken with the first wire earthed when the second was being heated, in addition to the cases in the previous experiments. The results are shown in the following table.

It will be noticed that the two numbers obtained with  $-200$  volts only differ by two per cent. No importance is to be

Potential of First Wire while Second Heated.	Activity Induced in First Wire.
-200 volts.	134
+200 "	27
-200 "	137
0 "	15

attached to the difference between the values (27 and 15) obtained with +200 and 0 volts respectively.

The numbers on page 532 show that the activity induced by heating the second wire falls off fairly rapidly with time when the first wire is heated. There is, however, no evidence to show that the induced activity falls off with time if the first wire is allowed to remain cold. A definite experiment was made to test this point by allowing the first wire to remain cold for 75 minutes after the second had been heated. On now raising the temperature of the first wire to that at which it previously gave no leak with +200 volts, 45 divisions per minute were obtained. This current was practically equal to that which would have been obtained if only two or three minutes had been allowed to elapse.

The next point that was investigated was to see if a wire which had lost the power of discharging positive electrification could not be revived by other methods than by charging it negatively in the neighbourhood of a second hot wire. Of these methods the effect of air will be considered first.

#### *The Activity induced by Air.*

To test this advantage was taken of a small leak in the apparatus which caused the pressure to increase by about  $\frac{1}{10}$  mm. in twelve hours. The first wire was heated on the afternoon of August 7th by .280 ampère, and the leak with +200 volts was found to be 1 division per minute at .0023 mm. pressure. On the following morning the pressure had risen to .16 mm., and the leak under the same conditions as before was found to be 45 divisions per minute. The leak induced by air in this way was found to fall off very rapidly with the time. This is readily seen from fig. 5 (Pl. IX.), where the induced activity in scale-divisions per minute has been plotted

against the time the wire has been heated (in minutes). It will be seen that there is practically nothing left after 5 minutes' heating.

Another case where .08 mm. of air was let into the apparatus suddenly gave a higher rate of leak, viz. 382 divs. per minute in the units which have so far been employed in this paper. The actual readings and the times are given in the following table :—

+ ve Leak cc .	Time.
	min. sec.
154	0 15
78	0 54
32	1 15
18	1 45
17	2 30

Here again it is evident that the induced activity is not very persistent.

The apparatus was now taken down and the wire allowed to remain exposed to air at atmospheric pressure for several days. On reducing the pressure to .001 mm. and keeping the wire at +200 volts a leak of 160 divs. per minute was obtained even when the wire was only heated with .228 amp. The heating current was now raised to .240 ampere, and the following values of the current were obtained at the times stated. The pressure was .0007 mm.

+ ve Leak cc .	Time.
	min. sec.
255	0 10
19	4 15
4	8 10
2	13 10
.7	23 0

In this case also there is practically no effect left after heating the wire to a given high temperature for some five or six minutes.

*Activity Induced by Hot Wires at Higher Pressures.*

Practically all the preceding experiments with the two-wire system were made at pressures of about a thousandth of a millimetre. In order to see if the effect was obtained at higher pressures a glass tap was added to the apparatus so that any desired quantity of gas could be introduced. The induced activity was very marked at  $\cdot 38$  mm.; since heating the second wire for 2 mms., the first being kept at  $-200$  volts, produced an initial current of 348 scale-divisions per minute. This induced activity was found to die away much more slowly than that produced by air and measured at a lower pressure, as the following numbers indicate :—

+ ve Leak $\alpha$ .	Time.
	min. sec.
173	0
145	3 15
115	6 30
91	9 0
70	12 0
58	15 0
34	24 0
22	32 0
12.5	45 0
8	70 0
3.5	130 0

The logarithms of the values of the induced leak, obtained by subtracting three from the numbers in the above table, are plotted against the time in fig. 6. It will be observed that all the points fall very nearly in a straight line, showing that the transferred activity follows the same law of decay as the original activity of the wire.

The high values of the induced activity given above were now obtained every time. A repetition of the experiment, in which the second wire was only heated for one minute, gave an initial leak of 200 divisions in 15 seconds.

The pressure was now reduced to  $\cdot 055$  mm., and the experiments repeated. Heating the second wire for thirty seconds was now found to give an induced activity of 332

divisions per minute. The way in which the current fell off with the time is shown in the following table :—

+ve Leak $\alpha$ .	Time.	
	min.	sec.
154	0	15
18	4	0
9	8	0
6	11	15
4	22	0

It appears from these numbers that the rate of falling off is greater than at higher pressures. The difference may, however, be due to a difference in the temperature of the wire in the two cases.

*Activity induced by the Luminous Discharge.*

In making experiments to see if the induced activity was increased by increasing the potential-difference between the two wires, it was found that an extraordinarily big effect was obtained with  $-400$  volts on the first wire. When the experiment was repeated it was found that an ordinary vacuum-tube discharge had been passing between the two electrodes. Further experiments were therefore made with both electrodes cold in order to see if the discharge produced the effect even when the second spiral was not heated.

The first wire was heated in the usual way until it gave no leak with  $+200$  volts and a heating-current of  $\cdot 35$  ampere. It was then allowed to cool, and raised to a potential of  $-400$  volts, the second wire being earthed. This difference of potential was sufficient to produce a discharge which was allowed to pass between the two electrodes for 60 seconds. After waiting a few minutes the first wire was heated to the same temperature as that at which it had been tested before, and the leak was measured with  $+200$  volts on the first wire. An induced activity of 500 divisions in 30 seconds was observed.



It was evident, as in the former case, that this effect was not due to ions left in the gas by the discharge, since there was no leakage of electricity from the first wire until it was heated.

An experiment was next made to see if the induced activity would persist for 40 minutes if the wire was kept cold after passing the discharge. As before, the wire was tested and found not to leak with .35 ampere of heating-current. It was then cooled and the discharge passed for 60 seconds. After waiting 40 minutes the wire was heated with .35 ampere, and charged to +200 volts as before. The induced activity was now found to be somewhat over 500 divisions in 40 seconds, and was therefore, within experimental errors, equal to that found when the wire was tested immediately. The activity induced by the discharge therefore falls off very slowly, if at all, by simply keeping the wire cold.

In all the preceding experiments, the wire which had been made active was the negative electrode. Experiments were now made to see if any activity was induced in this wire when the discharge was passed in the opposite direction, and if so what the relative magnitude of the induced activity was in the two cases.

The results show that the activity induced on the positive electrode is only about one-fifth of that induced on the negative, but that nevertheless it is quite marked and definite.

Electrode on which Activity Induced.	Induced Activity.
+	176
-	1200
+	280

It is to be noted that the ratio of the effects in the two directions is practically equal to that found for the corresponding effects produced by the discharge from hot wires and given on pp. 532 and 533. It seems probable therefore that the two phenomena are intimately connected.

The fact that activity could be induced both by the positive leak from hot metals and by the ordinary discharge led to the view that it was due to positive ions which stuck to the electrode and formed a double layer. In this case the same effect ought to be produced whenever positive ions discharged to the surface of the metal.

With the view of testing this supposition careful experiments were made to see if collecting positive X-ray ions on a wire increased the leak from it at a given temperature at atmospheric pressure; but no effect was obtained. A similar result was got at a low pressure. It was thought that these negative results might be due to the X-rays themselves possibly having the power to destroy the induced activity. This was the more probable, since X-rays are well-known to have a very intense action on metallic surfaces, resulting in the production of secondary rays; but on exposing a wire, which had been made strongly active, to the rays, no diminution of the induced leak was obtained.

### *Conclusion.*

The experiments which have been described show that the positive leak from a hot platinum wire at low pressures is not a definite function of the temperature, but that it gradually decays with time. The complexity of the phenomena seem to indicate that in general the ionization is produced by more than one substance; but where one effect is predominant the rate of decay of the leak is proportional to its value at the time considered. At a constant temperature the induced leak thus falls away as a negative exponential function of the time.

Further, a wire which has been heated at a given temperature until it has lost the power of discharging positive electricity, may have that property restored to it by any of three agencies. These are:—(1) Exposure to air; (2) exposure to the positive discharge from a second hot wire; and (3) making it an electrode during the passage of a luminous discharge.

The first and third methods lead to the conclusion that the effect is due to gas. This gas must, however, be in a peculiar

state since the experiments show that none of it comes off the wire negatively charged. In the case of the second and third methods the induced activity is much greater when the wire is made the negative electrode. This might indicate that it is due to the positive ions; but this supposition is rendered untenable by the fact that Röntgen-ray ions produce no effect. The fact that the discharge induces more activity on the negative than on the positive electrode leads to the conclusion that there are more gas molecules in the state necessary to produce the effect in the neighbourhood of the negative than in that of the positive electrode.

These effects have been shown to happen between  $\cdot 001$  and  $\cdot 3$  mm. pressure, but there is no reason to believe that similar phenomena would not occur at higher pressures.

When a "revived" wire is heated at a constant temperature the induced activity is gradually dissipated. In every case the activity fell off in such a manner as it would if the rate of decrease were proportional to the activity momentarily present. In fact the phenomenon is exactly analogous to a monomolecular chemical reaction. The quantity which corresponds to the velocity of the reaction is probably a function of the pressure of the gas and of the temperature of the wire.

In air at atmospheric pressure the falling off of the conductivity with time is much slower than at low pressures. Thus Mr. H. A. Wilson\* found the following numbers for the current in amperes between two coaxial platinum cylinders at the temperatures stated. The potential-difference was 800 volts and the outer tube was negative.

Temperature 800°.	900°.	1000°.	1100°.
July 6..... $8 \times 10^{-6}$	$40 \times 10^{-6}$	$120 \times 10^{-6}$	$400 \times 10^{-6}$
July 10..... $2 \times$ „	$11 \times$ „	$50 \times$ „	$140 \times$ „
July 30..... $\cdot 1 \times$ „	$\cdot 7 \times$ „	$2\cdot 5 \times$ „	$8 \times$ „

\* Phil. Trans. vol. cxcvii. p. 415.

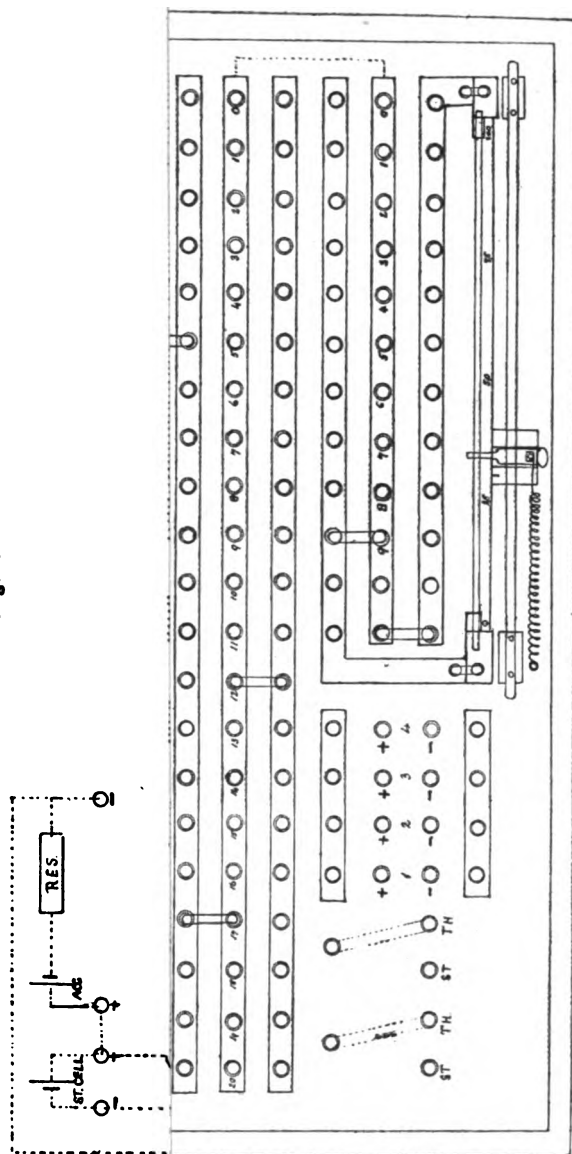
The greater persistence of the positive leak at high pressures is probably to be attributed either to the greater difficulty experienced by the induced activity in diffusing away, or by the fact that a new active layer is continually being reformed on the wire. Which of these two views is correct is a matter for future experiment to decide. In the present experiments the induced activity appeared to be more persistent at  $\cdot 3$  mm. than at  $\cdot 06$  mm.

The activity induced by the luminous discharge, and several other points which are not definitely settled in this communication, are being further investigated at present.

The experiments were carried out in the Cavendish Laboratory, and the author's best thanks are due to Professor J. J. Thomson for his kindly interest and advice during the course of the work.

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**Fig. 1.**





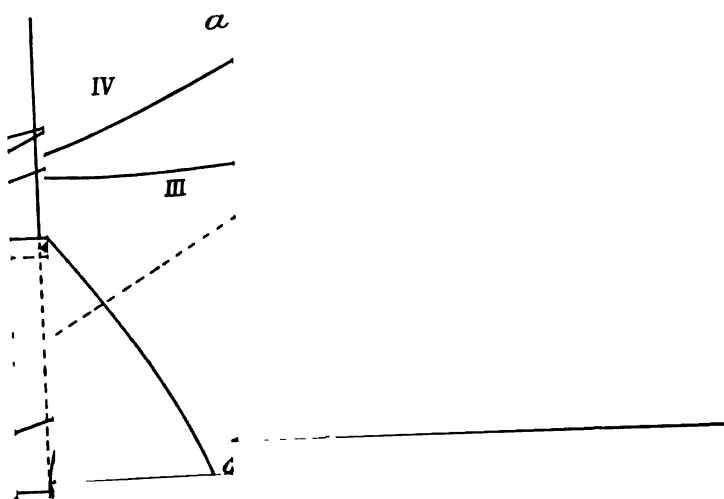






FIG. 5.

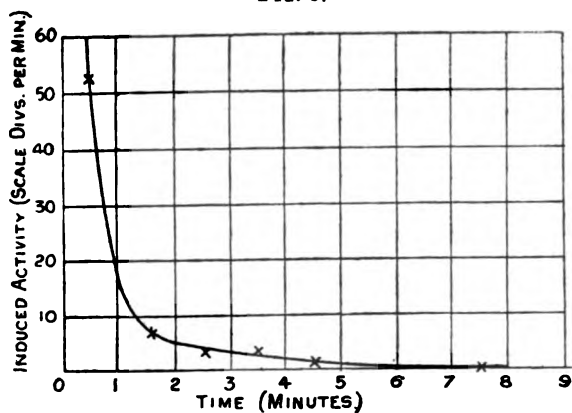
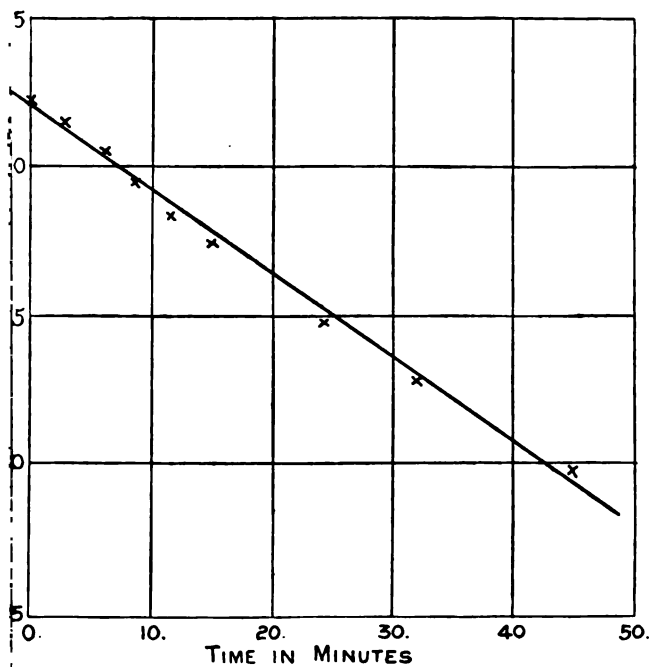


FIG. 6.





LIV. *The Vapour-Densities of some Carbon Compounds; an Attempt to Determine their correct Molecular Weights.* By SIR WILLIAM RAMSAY, K.C.B., F.R.S., and BERTRAM D. STEELE, D.Sc.\*

[Plate X.]

THE accurate determination of the densities of gases has been for long an object to which chemists have paid attention. On the other hand, the density of vapours has only been roughly estimated, as a means of arriving at a conclusion regarding molecular weights; whilst accurate molecular weights have been deduced from the results of analysis, and from previous determinations of atomic weights.

Every method which brings additional evidence to bear on so important a class of constants as atomic weights must be welcome; and it was with great interest that the memoirs of M. Daniel Berthelot were perused, "*Sur la détermination rigoureuse des poids moléculaires des gaz en partant de leurs densités et de l'écart que celles-ci présentent par rapport à la loi de Mariotte* (*Comptes rendus*, 1898, xii. pp. 954, 1030, 1415, & 1501). In these papers M. Berthelot has brought Regnault's determinations of the compressibility of hydrogen, nitrogen, oxygen, and carbon monoxide between one and six atmospheres to bear on determinations of their density by M. Leduc, in such a manner that their relative weights can be compared when, if Avogadro's hypothesis be granted, equal volumes contain equal numbers of molecules. In the case of the elementary gases, oxygen, hydrogen, and nitrogen, inasmuch as the molecules are diatomic, the determination of the molecular weight is at the same time a determination of the atomic weight; and with carbon monoxide the atomic weight of carbon is arrived at by simple subtraction. To quote Berthelot's words: "*Le volume moléculaire d'un gaz à 0° et sous la pression atmosphérique étant égal à 1 pour un gaz qui suivrait exactement la loi de Marriotte, ce volume a la valeur 1— $a$  pour un gaz qui ne la suit pas.*" The definition of  $a$  is that given by Regnault, viz.  $\frac{p_0 v_0}{pv} - 1 = a(p - p_0)$ , and

\* Read December 12, 1902.

represents the deviation of the compressibility of the gas from Boyle's law for increase of pressure of one atmosphere. The error in the atomic weights of oxygen, hydrogen, nitrogen, and carbon thus determined is estimated not to exceed 1 part in 5000. M. Berthelot also discusses deviations from Boyle's law exhibited by easily liquefiable gases, namely, carbon dioxide, nitrous oxide, hydrogen chloride, acetylene, phosphoretted hydrogen, and sulphur dioxide, making use for this purpose of van der Waals' modification of the simple gas laws. From the previously determined densities of these gases he calculates their molecular weights, using as a basis the molecular weight of oxygen taken as 32; whence by subtraction the atomic weights of hydrogen, carbon, nitrogen, sulphur, and chlorine are deduced.

Another method of applying M. Berthelot's procedure is this:—Determine the density of the gas; determine also its compressibility at low pressures, preferably below one atmosphere; assuming the compressibility to be a linear function of pressure, calculate the value of the product  $pv$  at zero pressure: the ratio of the  $pv$ 's will be the ratio of the densities when equal volumes contain equal numbers of molecules. The molecular weights, and consequently the atomic weights, follow as a matter of course. The method can also be applied graphically, by plotting as ordinates the pressure, and as abscissæ the values of  $pv/T$ ; where the curve cuts the line of zero pressure the theoretical value of  $pv/T$  has been reached.

There appeared every prospect that the determination of the density of vapours should, if carried out with pure substances, lead to results as interesting and important as those deduced by Daniel Berthelot. And if the estimations were made with pure substances the atomic weights of the elements contained in the compounds might be determined with extreme accuracy. Moreover, the method of deducing atomic weights from density may be regarded as a "statical" method, in contrast with the usual analytical methods, which, on account of the transformations which the elements are made to undergo during the determination, may well be termed "dynamical."

After some preliminary attempts to apply a modification of

Dumas' method it was discarded in favour of a modification of Gay-Lussac's; this method has the advantage that while densities are being determined compressibilities may be simultaneously estimated with the same sample of material, at least within certain limits. But for low pressures separate estimations of compressibility were made with a special apparatus designed by one of us for the purpose (*Trans. Chem. Soc.* 1902, vol. lxxxi. p. 1176). We had intended to investigate the molecular weights of a number of substances containing various elements; but the results which some compounds of carbon and hydrogen, and of carbon, hydrogen, and oxygen have led to are so remarkable that it appears desirable not to delay publication. We may here anticipate our conclusions, in order that the importance of each point may not be overlooked. Our evidence goes to show that the densities of certain compounds calculated for zero pressure are not proportional to their molecular weights deduced from the atomic weights of the elements which they contain. This conclusion involves one, or it may be several, of the following assumptions:—

1. The substances employed may not have been pure;
2. The methods of experiment may not be capable of giving sufficiently accurate results;
3. Avogadro's hypothesis may not hold for vapours for one of the reasons below.
  - (a) The vapours may adhere to the glass and increase their apparent density;
  - (b) The vapours may contain some complex molecular groups, or, in other words, they may display partial molecular association at the temperature of experiment, even under very low pressure;
  - (c) The atomic weights of the elements may alter their values according to the ratios between the number of atoms in the compounds.

The first two suppositions, until disproved, are of course by far the most likely, and we shall therefore commence with a description of the sources and preparation of the compounds under experiment, in order that our readers may be in a position to judge of their probable purity.

*Preparation of the Compounds.*

These were: hexane, two octanes, benzene, toluene, ether, and methyl alcohol. The first three we owe to the kindness of Prof. Sydney Young. Beyond drying them with phosphoric anhydride and distilling them into our weighing-bulbs they underwent no process of purification.

1. *Normal hexane* (Young, *Trans. Chem. Soc.* vol. lxxiii. pp. 910-913).—This specimen was fractionated from petroleum ether. The fractionation was carried out with a combined regulated temperature still-head and six-column dephlegmator. The separate fractions were heated with fuming nitric acid for several days, and after treating with potash, and drying, they were distilled. The comparison of the constants is as follows:—

	Petroleum.	Normal hexane from Propyl iodide.
Boiling-point.....	68·95°	68·95°
Density at 0°/4° (four fractions afterwards mixed together)..	0·67693 0·67699 0·67697 0·67702	0·67697
Critical temperature.....	234·8°	234·8°
„ pressure .....	22540 mm.	22510 mms.

The concordance of these results affords a guarantee of the almost absolute purity of the specimen.

(2) *Normal octane* (Young, *ibid.* xvi. p. 166).—This sample was made from octyl iodide by Kahlbaum. Its boiling-point at normal pressure after purification by Young was 125·8°. It was collected in three fractions, which showed the densities A, 0·71850; B, 0·71847; C, 71848. These fractions were mixed. The boiling-points, determined at different times, were 125·8°, 125·85°, and 125·75°.

(3) *Di isobutyl* (Young, *ibid.* xvi. p. 165).—Made by Young and Miss Fortey by treating isobutyl bromide with sodium in ethereal solution. “No great difficulty was experienced in the preparation of di-isobutyl, and the yield was fair. As the boiling-point of the paraffin (109·2°) is considerably higher than that of isobutyl bromide (92·3°), it could be separated fairly completely from the unaltered bromide by fractional distillation. The final purification

was effected by treatment with a mixture of nitric and sulphuric acids, and subsequent fractional distillation through a twelve-column Young and Thomas dephlegmator. Owing to the partial conversion of the isobutyl bromide into the tertiary bromide a small quantity of hexamethyl-ethane is formed; but this is completely removed during the fractional distillation." The boiling-points of three fractions were  $109.2^{\circ}$ ,  $109.2^{\circ}$ , and  $109.25^{\circ}$ ; the density at  $0^{\circ}$  was 0.71021: Schiff found 0.7103.

The remaining substances were prepared by ourselves.

(4) *Benzene*.—A sample of Kahlbaum's purest thiophene-free benzene was twice subjected to fractionation; the boiling-point was absolutely constant.

(5) *Toluene*.—Sample A was prepared from paratoluidine by diazotization. Its boiling-point was constant. Sample B was synthesized from bromobenzene and methyl iodide; the constant boiling fraction was crystallized. As the process of crystallization at very low temperatures has, so far as we are aware, not been described, a short account of it may prove interesting.

Some ordinary crude toluene was cooled by pouring liquid air into it until it was partially solid. The purified toluene was introduced into a tube into which was sealed an inverted filter, plugged with cotton-wool. On dipping this tube into the cooled toluene the pure toluene slowly froze, forming large crystals; when about one-third had frozen the unfrozen portion, containing any possible impurities, was filtered off. The crystals when melted formed the sample termed B.

(6) *Ether*.—Prepared from absolute alcohol in the usual way. It was then fractionated from phosphorus pentoxide until the boiling-point was constant. The samples of ether were treated in three different ways: sample A was distilled from phosphoric anhydride into the bottle in which it was preserved; sample B was a portion of A which had been allowed to stand for three days over phosphoric anhydride, and then shaken with mercury to remove possible ethyl peroxide; it was then distilled into the weighing-bulb from pentoxide by a method to be described. As samples A and B both gave the same puzzling density, and as it was possible that the methods of purification left something to be

desired, sample C was a portion of B which was frozen in a manner similar to that described for toluene. It was cooled in a tube immersed in frozen crude ether until the ether in it had crystallized. The large clear crystals, some of which were two inches long, were separated from twice their volume of mother-liquor by upward filtration. The crystals when melted formed sample C.

(7) *Methyl alcohol*.—Methyl oxalate was prepared from "pure" methyl alcohol. The crystallized oxalate was washed with water until the washings gave no iodoform reaction. The ester was decomposed with potash, and the alcohol dried with lime of very high quality, which reacted violently and at once with water. The sample was re-distilled with lime until the boiling-point became constant.

It is constancy of boiling-point, and not temperature, which we regard as a criterion of purity. To register a really accurate temperature is a difficult undertaking, and one which was unnecessary for our purpose.

#### *Temperatures of Experiment.*

These were approximately 100°, 115°, and 130°. They were obtained by surrounding the tubes to be heated with the vapour of pure chlorobenzene, which had been very carefully fractionated so as to ensure a constant boiling-point, boiling under correspondingly reduced pressures. The arrangement did not materially differ from that described in the *Trans. Chem. Soc.* 1885; all the joints were sealed so that no leakage occurred, and temperature could be recovered from day to day within 1/100 of a degree.

As the standard of comparison for the densities of the substances mentioned above was oxygen, its density at these temperatures was required. Instead of a direct determination of the densities of oxygen at these temperatures, however, the coefficient of expansion of the gas between 0° and 130° was directly measured with an unknown weight; it was found to be  $1/272.52 = 0.0036694$ . The mean of the determinations of the weight of one litre of oxygen at 0° by Regnault, Jolly, Leduc, and Rayleigh was accepted as the basis of calculation, namely, 1.42961.

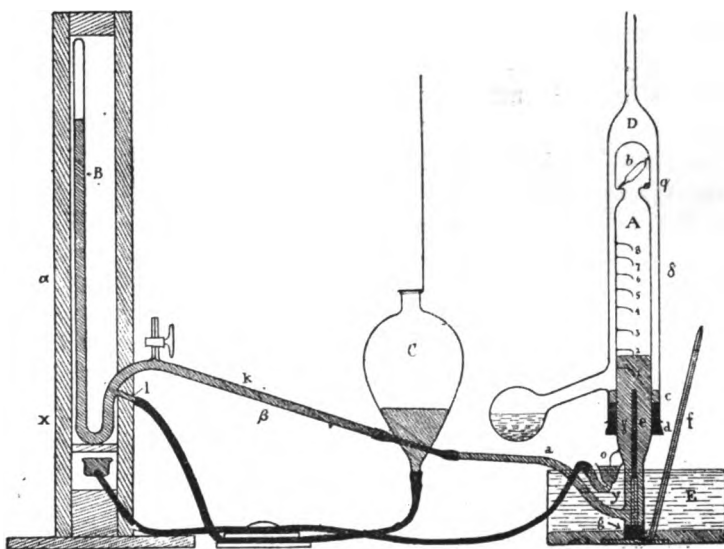


As the coefficient of expansion of oxygen was determined by a method practically identical with that employed for the measurements of densities, it will be more convenient to defer the description of these experiments until an account of the apparatus has been given.

*Description of Density-apparatus.*

The apparatus consists essentially of the volume-tube and pressure-gauge A and B (fig. 1) which are connected by a short piece of thick-walled india-rubber tubing. The volume-tube A consists of a glass tube of about 20 mms. diameter

Fig. 1.

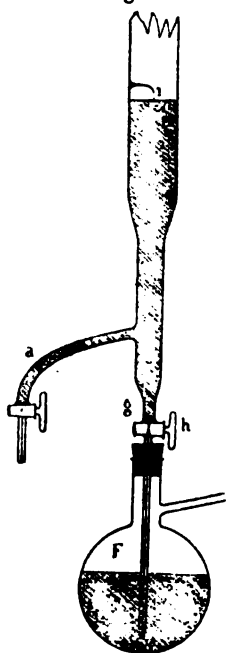


and about 780 mms. in length, constricted at its lower end, near which is attached the side-tube *a*. The top is blown into a cap *b* of the form shown in the figure; this serves the double purpose of trapping the weighing-bulb after its insertion, and also of retaining a small globule of mercury. The bulb is thus prevented from floating on the surface of the mercury in *A*, and from breaking off the glass points 1, 2, 3, &c. The globule of mercury gives off vapour when the tube is heated, and the space rapidly becomes saturated with

mercury-vapour; experiments have shown that if this precaution be omitted the pressure of mercury-vapour takes many hours to rise to its maximum, on account of its great density, and consequent slow rate of diffusion.

The whole tube is inclosed in a jacket D, which contains during the experiment the vapour of chlorobenzene; and D is attached to the apparatus for regulating the pressure under which the chlorobenzene boils. The whole system of tubes rests on its cork *g* in mercury, contained in a vessel E, through which water is made to circulate. The temperature of the volume-tube A, from its top to where it enters the mercury *c*, required to protect the rubber cork *d* from being attacked by the hot chlorobenzene, is that of the chlorobenzene vapour, that of the portion standing in water is also known, and that of the intermediate portion is determined by means of a thermometer with a long bulb *e*, of the same

Fig. 2.



length as the portion of tube of unknown temperature; the temperature is thus integrated between the point *c* and the surface of the water. The temperature is read on the stem *f*.

The volumes of the vapour are determined by adjusting the surface of the mercury to a set of points 1 to 8, of blue enamelled glass, which should be ground on a whetstone with oil in the manner recommended by Lord Rayleigh. To determine once for all the volumes indicated by the different points stopcocks were sealed to the end of the tube at *g* and to the end of *a*, as shown in fig. 2. The tube was completely exhausted with a Töpler pump, and filled with warm mercury; by attaching a Fleuss pump to the exit of the weighing-flask F the mercury flowed out through the capillary end of the stopcock *h* into F. The mercury was drawn below the level of the point 1 in

question; the Fleuss pump was disconnected from F, and by turning the stopcock rapidly the mercury rose until it

nearly touched the point. Adjustment was made by help of a single lens. During calibration the whole tube was surrounded with water of known temperature. The average error was about  $1/30,000$  of the total volume.

After calibration the next step was to determine the vertical distance between points 1 to 8 and a point 0 (fig. 1) attached to the outside of the tube below the jacket. The volume-tube was set up opposite the scale B, and made vertical with a plumb-line, and the distances read with a telescope to within 0.02 mm. In order to correct these differences the linear expansion of the glass was required; as a sufficient approximation the cubical expansion of this sample of glass (0.000029) was determined, and one-third taken as the linear expansion. The cubical expansion was, of course, also required to correct the read volumes.

The manometer consisted of a glass U-tube B, 100 cms. long and 13 mms. in diameter. It was filled with mercury and boiled out *in vacuo*. This gives no trouble provided the tube is carefully freed from dust by washing out with bichrome and sulphuric acid, and subsequently with distilled water, before drying it. The side-tube *k* is provided at the highest point with a stopcock through which any bubbles of air can be displaced. The short limb of the U-tube is connected by means of the side-tube *l* and thick-walled rubber tubing with the mercury reservoir C. Final adjustment of the mercury surface to the points in the volume-tube A is made by means of a squeezer, consisting of two pieces of wood and a screw. The manometer was water-jacketed, a delicate thermometer being inclosed in the jacket. The scale was obtained from Zeiss. It was tested by means of a travelling microscope, reading to 0.001 mm., and was found to be consistent to 0.03; a table of corrections was made by which readings were corrected to within 0.01 mm.

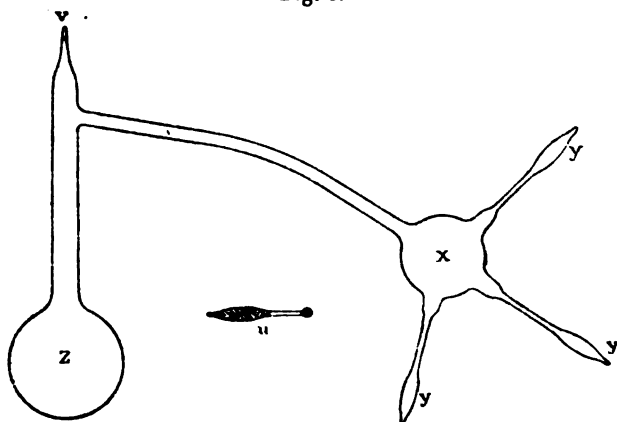
In order to prevent the expansion of the scale the hot volume-tube stood at some distance, and the level was "carried" from the external point on the volume-tube to the scale by means of two mercury cups and a connecting tube. The cups were placed fairly level by eye, and mercury was poured in until the meniscus stood just a trace below the level of the point. By means of a squeezer, compressing the indiarubber tube which connected the two mercury cups,

the level of the mercury was so adjusted as accurately to touch the point. The level of the mercury on the scale was the same, and readings could be made of the distance between the external point, and consequently of all the internal points, and the height of the mercury in the manometer.

The reading of the levels of mercury in the cup and in the manometer was made with a telescope standing at a distance of 10 feet. By a simple device due, we believe, to Prof. Poynting, readings to an accuracy of 0.01 mm. were easily made. It consists of a piece of truly plane parallel glass in front of the telescope which can be rotated through an angle by means of an attached pointer. The rotation of this plane glass displaces the object viewed; it is easy to count the divisions on an arc, ruled in sine divisions, which correspond to 1 mm. of the scale, and in this way hundredths of a millimetre may be directly and simply estimated. The device offers a simple and inexpensive substitute for a cathetometer, and is not behind one of the best in accuracy.

In order to prevent absorption of moisture during the filling of the bulbs this operation was carried out *in vacuo* by means of the apparatus shown in fig. 3. The small bulb *x* is about 2 cms. in diameter, there are sealed to it a number of

Fig. 3.



small weighing-bulbs *y*; *x* is attached by the tube to a somewhat larger bulb *z*.

After this apparatus is made a small quantity of phosphoric anhydride is introduced into *z*, and the whole is exhausted and sealed at *v*. It is then allowed to stand for a length of time so that all moisture introduced in making and sealing the apparatus may be absorbed; the point *v* is then broken and the liquid with which the bulbs are to be filled is introduced; the apparatus is again exhausted and again sealed at *v*. Finally, after the liquid has stood in contact with the anhydride for a number of hours, a portion of it is distilled over into *x*, and so into the bulbs *y*; these are sealed off in such a manner by a fine blow-pipe flame that a long capillary stem remains attached to *y*, containing no liquid or foreign gas, but only the vapour of the contained liquid. The size which *y* should possess for a given substance is calculated approximately from the molecular weight and density of the liquid in question; after sealing off the point of the stem is melted so as to form a knob about 1 or 2 mms. in diameter, and a nick is made with a glass-cutter in the capillary about 1 cm. from the end. (The filled bulb is shown in fig. 3, *u*.) In the case of methyl alcohol lime was substituted for phosphoric anhydride.

#### *The Limits of Accuracy.*

The accuracy of the final result depends on the measurements of four quantities, namely, the pressure, the volume, the temperature, and the weight of substance introduced into the volume-tube. The smallest pressure that has been measured with this apparatus is 220 mms. The divisions of the scale employed, when corrected by the calibration table previously referred to, are consistent to 0.01 mm. The pressures given in the tables on subsequent pages are the differences between two readings on the scale, each of which is the mean of three independent readings for which the surface of the mercury is re-set to the point under observation. In no case did the eight settings differ by more than 0.05 mm., whilst in the great majority of cases they lie within 0.03 mm.; so that the extreme error due to reading of pressure may be taken as about 0.05 mm., or about 1 in 4000. As will be seen from the curves and tables given

later it is only occasionally that a point is found to diverge so widely from the curve.

The error arising from the determination of the volumes in the tube A is negligible; this is seen from the following result of a calibration carried out in duplicate:—

	February 16th.	March 5th.
I. . . .	228·947	228·962
II. . . .	201·866	201·856
III. . . .	179·473	179·463
IV. . . .	156·399	156·379
V. . . .	114·734	114·742
VI. . . .	95·171	95·167

The temperature of the vapour-jacket can easily be maintained constant to within  $0\cdot02^{\circ}$  by occasionally adjusting the pressure under which the liquid boils; this has been repeatedly tested and proved during the course of the research. The temperature at which the majority of the experiments were carried out was  $130^{\circ}$ ; the absolute temperature was therefore about  $403^{\circ}$ , and a variation of  $0\cdot02^{\circ}$  would therefore amount to only 1 part in 20,000.

The weighings were made with a long-beam Oertling's balance which, on reading by oscillations, recovered weighings correct to within  $0\cdot00002$  gram; duplicate weighings of one of the toluene and of one of the methyl-alcohol bulbs will serve to illustrate the accuracy that could be attained by careful weighing:—

	Toluene.	Methyl-alcohol.
I. . . .	$0\cdot77528$ gram	$0\cdot39244$ gram
II. . . .	$0\cdot77527$ „	$0\cdot39242$ „

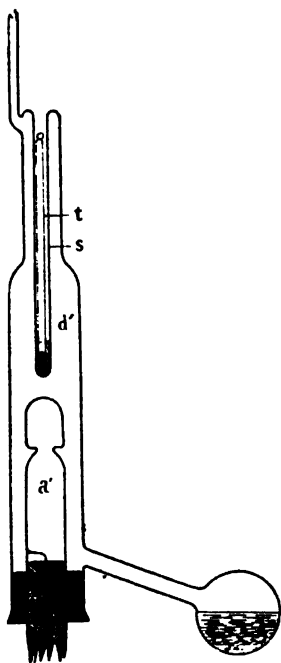
As, however, each experiment involved two weighings, one of the full and one of the empty bulb, the total error was probably about one twenty-fifth of a milligram, or  $0\cdot00004$ . Since the average weight of substance taken was about  $0\cdot15$  gram the error should be about 1 in 4000; and this is about the degree of concordance which has been found in cases in which more than one experiment with the same substance has been carried out.

*The Coefficient of Expansion of Oxygen.*

As already explained it was necessary to determine this coefficient in order that the densities of the vapours might be compared directly with that of oxygen. What was done practically was to express the temperature of the experiment in terms of an oxygen thermometer.

The actual densities of the various vapours were determined at three temperatures, namely, the temperatures of chlorobenzene boiling under a pressure of 292.75 mms., 468.5 mms., and 719.0 mms. of mercury. In order to ascertain these temperatures the pressure exerted by a constant volume of oxygen was measured, first at the temperature of melting ice; second at 99.82°, the temperature of water boiling under a pressure of 755.1 mms.; third, at the temperature of chlorobenzene boiling under a pressure of 292.75 mms.; and lastly with chlorobenzene under a pressure of 719.0 mms.

Fig. 4.



For this purpose the portion of the apparatus A and D (fig. 1) was replaced by that shown in fig. 4, where  $a'$  is a smaller tube, the volume of which was about 92 c.cs.; this tube was dried very carefully, filled with warm dry mercury, and the mercury was displaced with perfectly dry oxygen which had been prepared by the decomposition of potassium permanganate. The tube  $a'$  was then connected with the manometer, after the thermometer  $d'$  had been inserted. It was next jacketed successively with chlorobenzene, with water, and with ice.

For each measurement a number of readings were made,

which are given later on. It is necessary first to explain the various corrections that have to be applied to the actual readings.

These will best be understood by aid of the Greek letters on fig. 1.

Section  $\alpha$ , the manometer column, is surrounded with running water, the temperature of which is observed; a correction must here be applied to reduce the height of the mercury column to its height at  $0^\circ$ . This correction is given in the table under  $a$ .

Section  $\beta$ , forming the connecting tube between manometer and volume-tube, is not jacketed; but its vertical height is small, and an error of even a few degrees in its temperature is unimportant; the correction is given under heading  $b$  in the table.

The temperature of  $\gamma$ , the lower portion of the volume-tube, is ascertained by means of the long-bulbed thermometer previously described, and its correction is given under heading  $c$ ; the temperature of  $\delta$ , its upper part, is that of the vapour-jacket, and the correction is given under heading  $d$ . Corrections for the portions  $x$  and  $y$  are not so important since  $x$  is small, and since the two limbs of  $y$  are of the same length and at the same temperature. A constant correction of a few hundredths of a millimetre was made for section  $x$  when the temperature of  $\alpha$  was much lower than that of the room.

Further corrections have to be applied for depression due to capillarity in the manometer-tube, and for vapour-pressure in the volume-tube; the former of these is already applied to the figure given under the heading "manometer." Hence, if the actual reading of the manometer is  $m$ , its true height is  $m - a - b - e$ , where  $e$  is the correction due to vapour-pressure of mercury in the volume-tube. From this has to be subtracted the height of the mercury in the volume-tube. The position of the external point 0 (fig. 1) is directly measured; to its height must be added the vertical distance between the points 0 and 1, plus the correction for linear expansion of the glass; point  $(0-1) + f$  gives the actual



height of the mercury which has to be corrected for temperature by subtracting the quantities  $e$  and  $d$ ; hence

Pressure corrected to  $0^\circ$

$$= (m - a - b - e) - (\text{point } 0 + \text{point } (0-1) + f - c - d),$$

$$= (m + c + d) - (\text{point } 0 + \text{point } (0-1) + f + a + b + e).$$

The pressures thus found must finally be corrected for the change in volume brought about by the cubical expansion of the glass; this correction is given under the heading  $k$ . For these experiments the correction applied to section  $x$  is 0.06 mm.

The jacket  $d'$  (fig. 4) was so constructed that it was possible to insert the delicate thermometer  $t$  into the inner tube  $s$ ; and it was thus possible to obtain the values of its graduations in terms of the oxygen scale.

TABLE I.

The Coefficient of the Expansion of Oxygen.

I. Temperature  $0^\circ \text{C}$ .

		A... length=542 mms.		temperature = $8.9^\circ$	
		B... " = 172 "		" = $15.8^\circ$	
		C... " = 118 "		" = $7.8^\circ$	
		D... " = 16 "		" = $0.0^\circ$	
Manometer	(1) 719.33	(2) 719.34	Point 0	(1) 21.51	(2) 21.50
+ $c$	" 0.17	" 0.17	+point(0-1)+ $f$	" 113.79	" 113.79
+ $d$	" 0.00	" 0.00	+ $a$	" 0.84	" 0.84
+0.06	" 0.06	" 0.06	+ $b$	" 0.49	" 0.49
			+ $e$	" 0.00	" 0.00
X = 719.56		719.57		Y = 136.63	
				136.62	

Hence  $P = (X - Y) = (1) 582.93; (2) 582.95$ .

Mean pressure = 582.94.

II. Temperature that of water boiling at  $99.82^\circ$  under a pressure of 755.1 mms.

		A... length=752 mms.		temperature = $8.5^\circ$	
		B... " = 172 "		" = $17.4^\circ$ to $17.7^\circ$	
		C... " = 118 "		" = $48.0^\circ$ to $48.3^\circ$	
		D... " = 16 "		" = $99.82^\circ$	
Manometer...	(1) 929.79	(2) 929.81	(3) 929.84		
+ $c$	" 1.02	" 1.03	" 1.03		
+ $d$	" 0.29	" 0.29	" 0.29		
+0.06	" 0.06	" 0.06	" 0.06		
X = 931.16		931.19		931.22	

Point 0	(1)	21.22	(2)	21.22	(3)	21.25
+point(0-1)+f	"	113.84	"	113.84	"	113.84
+a	"	1.16	"	1.16	"	1.16
+b	"	0.54	"	0.55	"	0.55
+c	"	0.26	"	0.26	"	0.26
Y =		137.02		137.03		137.06
Hence P=(X-Y)=(1)		794.14;	(2)	794.16;	(3)	794.16
+k	"	2.30	"	2.30	"	2.30
True pressure	"	796.44	"	796.46	"	796.46
Mean pressure	=	796.453 mms.				

III. Temperature that of chlorobenzene boiling at 99.71° under a pressure of 292.75 mms.

A... length=752 mms.	temperature=	8.6°
B... " =172 "	"	=18.4° to 18.6°
C... " =118 "	"	=48.8° to 49°
D... " =16 "	"	=99.71°.

Manometer...	(1)	929.59	(2)	929.60	(3)	929.62
+c	"	1.04	"	1.04	"	1.04
+d	"	0.29	"	0.29	"	0.29
+0.06	"	0.00	"	0.06	"	0.06
X =		930.98		930.99		931.01
Point 0	(1)	21.21	(2)	21.23	(3)	21.23
+point(0-1)+f	"	113.84	"	113.84	"	113.84
+a	"	1.16	"	1.16	"	1.16
+b	"	0.57	"	0.57	"	0.57
+c	"	0.26	"	0.26	"	0.26
Y =		137.04		137.06		137.06
Hence P=(X-Y)=(1)		793.94;	(2)	793.93;	(3)	793.95
+k	"	2.30	"	2.30	"	2.30
True pressure	"	796.24	"	796.23	"	796.25
Mean pressure	=	796.24 mms.				

IV. Temperature that of chlorobenzene boiling under a pressure of 719 mms.=129.60°.

A... length=816 mms.	temperature=	8.1°		
B... " =172 "	"	= 17.2° to 17.4°		
C... " =118 "	"	= 58.6°		
D... " =16 "	"	=129.60°.		
Manometer ... (1)	993.65	(2)	993.62	(3) 993.60 (4) 993.64
+c	" 1.34	" 1.34	" 1.34	" 1.34
+d	" 0.37	" 0.37	" 0.37	" 0.37
+0.06	" 0.06	" 0.06	" 0.06	" 0.06
X =	995.42	995.39	995.37	995.41

Point 0	(1)	21.26	(2)	21.26	(3)	21.24	(4)	21.24
Point(0-1)+f	"	113.86	"	113.86	"	113.86	"	113.86
+a	"	1.19	"	1.19	"	1.19	"	1.19
+b	"	0.54	"	0.54	"	0.53	"	0.53
+c	"	1.12	"	1.12	"	1.12	"	1.12
Y	=	137.97		137.97		137.94		137.94
P=(X-Y)	=	(1) 857.45	(2)	857.42	(3)	857.43	(4)	857.47
+k	=	" 2.49	"	2.49	"	2.49	"	2.49
True pressure		" 859.94	"	859.91	"	859.92	"	859.96
Mean pressure = 859.93.								

From the above figures the coefficient of expansion of oxygen between  $0^{\circ}$  and  $100^{\circ}$  is found to be

$$0.0036694,$$

whilst the temperature of chlorobenzene boiling

at 292.75 mms. is  $99.71^{\circ}$ ;

and at 719.00 ,, is  $129.6^{\circ}$ ;

and from comparison with the thermometer in s, the temperature

at 468.5 mms. is  $114.9^{\circ}$ ,

all of them being expressed on the oxygen scale of temperature.

### *Method of Experiment.*

Before each experiment the volume-tube was carefully washed with distilled water and with pure alcohol and dried; it was then attached to a Töpler pump by means of an india-rubber cork, a tube containing phosphoric anhydride being interposed between the tube and the pump. The side tube  $\alpha$  (fig. 1) was attached by a short piece of thick-walled rubber tubing to a capillary tube, dipping into clean dry mercury; this rubber tube was closed by a screw clip. The volume-tube was then placed in a long glass jacket having a boiling-bulb sealed to one side near the lower end; it contained bromobenzene, and the vapour kept the tube at the temperature of  $160^{\circ}$  for a considerable time, during which it was from time to time exhausted by the pump. After cooling, mercury was allowed to enter through the capillary tube attached to  $\alpha$ , until the volume-tube was completely filled.

After this treatment no bubbles of air or gas are developed on heating to  $130^{\circ}$ , the temperature of experiment. The tube was then disconnected from the pump; the rubber stopper with the attached drying-tube removed, and the volume-tube was placed mouth downwards in a trough of mercury.

The previously weighed bulb containing liquid was then broken at the nick under the mercury, and the two portions of the tube were immediately inserted into the mouth of the volume-tube, into which they rise, and are trapped in the cap at the top.

On account of the bulb not being completely full of liquid nothing escapes; on the contrary, as soon as the tube is broken mercury rushes in and fills the capillary portion of the stem, which, as previously mentioned, contains only vapour at very low pressure.

The volume-tube is then removed from the trough, the mouth being closed by the finger, and placed in a nearly vertical position; the thermometer *e* is next inserted, and the side tube attached to the manometer. The jacket is slipped over the volume-tube, and after adjusting to verticality with a plumb-line the condenser-tube at the top of the volume-tube is sealed to the gauge-tube, and the pressure under which the chlorobenzene boils is adjusted.

During the experiment the bulb remains at the top of the volume-tube, along with a small globule of mercury; the latter gives off vapour quickly, and the heavy mercury-vapour falls and mixes with the vapour of the liquid; it is only in this manner that it is practicable to saturate the space with mercury-vapour without protracted delay.

After the experiment is finished the rubber tube joining *a* to *k* is clipped, disconnected, and attached to a flask in which a partial vacuum is made with a Fleuss pump; the greater part of the mercury is thus withdrawn from the volume-tube. The rubber tube is again clipped, disconnected from the flask, and attached to a capillary tube of very fine bore; on opening the clip air gradually enters the volume-tube without splashing up mercury. When the volume-tube is full of air the cork and thermometer are removed; any adhering globules of mercury are brushed away from its interior with a hair

pencil, and the two pieces of the bulb and the globule of mercury at the top are shaken out on to a clean plate; these are dried and weighed separately, and their volume deducted from the volume of the tube. To ensure accuracy the density of the sample of glass used to make the bulb was determined.

We have given a detailed account of all these operations because unless they are carried out in the manner described the experiment fails. It was only after many failures that the right method of manipulation was gradually evolved.

### *Experimental Results.*

A complete record of one experiment is given, with all the necessary corrections, in order that it may be perfectly clear how these are applied. It is, however, unnecessary to quote more than the final figures for the other experiments, because any arithmetical mistakes that might have been made in applying the corrections or in making the calculations were automatically detected on plotting the curves; many such cases have been found, but on interpreting the results graphically one point was found to lie off the curve, and on again going over the calculations it was always found to be due to a simple arithmetical slip.

In the annexed tables special sections are devoted to "Compressibility." It will be noticed that the pressures range, in these sections, from 40 mms. to about 200 mms. It would be impossible to weigh with sufficient accuracy, with the volume space practicable in such experiments, a quantity of substance which would yield the small amount of vapour necessary; hence the quantity of substance was only roughly measured. The curve of compressibility representing rise of  $p_v$  for decrease of pressure, therefore, is not continuous with the density curve; but if its position be shifted it forms a continuation of that curve. The shift in position is easily effected since the two curves generally overlap. The factor by which the compressibility numbers must be multiplied in order to make the two curves continuous is given in each case.

TABLE II.  
Methyl Alcohol. I.

Weight of substance = 0.08819 gram =  $m$ .

Volume corrections :  $-a = 0.176$ ,  $\beta = 0.099$ .  $(\alpha + \beta) = 0.275$ .

Temperature =  $129.60^\circ$ ; that of chlorobenzene boiling under 719.2 mms.

Length in mms. of  $A = (M - 177)$ ;  $B = 168$ ;  $C = 118$ .

Point .....	1	2	3	4	5
Length of D .....	21	86	138	195	246
Volume in c.cs. ....	228.962	201.856	179.463	156.379	134.656
$(\alpha + \beta)$ .....	0.275	0.275	0.275	0.275	0.275
$\lambda$ .....	228.687	201.581	179.188	156.104	134.381
	0.858	0.756	0.674	0.587	0.504
True volume .....	229.54	202.34	179.86	156.69	134.88
Temp. of A .....	$16.6^\circ$	$16.6^\circ$	$16.2^\circ$	$16.4^\circ$	$16.4^\circ$
" B .....	$18.5^\circ$	$19.0^\circ$	$18.7^\circ$	$19.0^\circ$	$19.0^\circ$
" C .....	$69.0^\circ$	$69.5^\circ$	$69.5^\circ$	$69.5^\circ$	$69.3^\circ$
Manometer .....	450.89	555.25	650.03	760.17	881.30
+ 0.06 .....	0.06	0.06	0.06	0.06	0.06
+ $c$ .....	1.47	1.48	1.48	1.48	1.48
+ $d$ .....	0.49	2.01	3.22	4.55	5.73
X = .....	452.91	558.80	654.79	766.26	888.57
Points .....	126.85	192.05	245.64	300.69	352.48
+ $f$ .....	0.11	0.18	0.23	0.29	0.34
+ point 0 .....	23.73	23.88	23.83	23.78	23.75
+ $a$ .....	0.82	1.13	1.38	1.72	2.06
+ $b$ .....	0.66	0.68	0.57	0.58	0.58
+ $e$ .....	1.10	1.10	1.10	1.10	1.10
Y = .....	153.17	218.92	272.75	328.16	390.33
P = (X - Y) .....	299.74	339.88	382.04	438.10	508.24
Pv/mT .....	1940.2	1939.2	1937.8	1935.7	1933.2

### Methyl Alcohol. II.

Weight of substance = 0.10427 gram. Temperature =  $129.60^\circ$ .

Volume in c.cs. ....	229.61	202.40	179.92	156.75
Pressure in mms. ...	363.82	401.19	451.01	517.11
Pv/mT .....	1937.6	1936.6	1935.3	1933.2

#### Compressibility.

Volume .....	32.162	19.267	12.279
Pressure .....	75.893	126.59	198.50
Factor .....	0.79735	0.79735	0.79735
Pv/mT .....	1946.2	1944.9	1943.5

Pv/mT at zero pressure = 1947.3.

\* In this experiment a sample of chlorobenzene was used as a jacket, which was afterwards found to be impure, for its boiling-point varied by some tenths of a degree; it also contained moisture.

## Ethyl ether, Sample A. I.

 Weight of substance = 0.17196 = *m*. Temperature = 129.6°.

Volume in c.c.s. ....	229.48	202.27	179.79	156.62	134.82	95.18
Pressure in mms. ...	256.06	287.08	322.68	370.00	429.24	605.48
<i>Pv/mT</i> .....	839.82	839.66	838.99	838.04	836.90	833.40

Weight of substance the same. Temperature = 99.71°.

Volume in c.c.s. ....	229.28	202.09	179.64	156.47	134.70	95.096
Pressure in mms. ...	234.21	265.57	298.47	342.06	396.74	559.38
<i>Pv/mT</i> .....	838.94	838.50	837.65	836.22	834.90	831.06

## Sample B. II.

 Weight of substance = 0.18303 gram = *m*. Temperature = 99.71°.

Volume in c.c.s. ....	229.21	202.02	179.56	156.41	134.63	95.024
Pressure in mms. ...	249.37	282.64	317.68	364.14	422.38	595.35
<i>Pv/mT</i> .....	838.97	838.10	837.32	835.99	834.66	830.37

## Sample C. III.

 Weight of substance = 0.15806 gram = *m*. Temperature = 129.6°.

Volume in c.c.s. ....	279.76	134.77	95.136
Pressure in mms. ...	296.84	395.03	557.61
<i>Pv/mT</i> .....	839.54	837.62	834.64

Compressibility at 129.6°.

Volume .....	57.394	30.274	18.136	11.551
Pressure .....	40.047	75.893	126.59	198.60
Factor .....	0.36678	0.36678	0.36678	0.36678.
<i>Pv/mT</i> .....	843.03	842.71	842.08	841.00.

*Pv/mT* at zero pressure = 843.45.

## Toluene. Sample A. I.

 Weight of substance = 0.22343 gram = *m*. Temperature = 99.71°.

Volume in c.c.s. ....	229.28	202.10	179.64	156.49	134.70
Pressure in mms. ...	242.03	273.88	307.70	352.07	407.33
<i>Pv/mT</i> .....	667.24	665.54	664.63	662.46	659.72

Weight the same. Temperature = 114.9°.

Volume in c.c.s. ....	229.37	202.18	179.72	156.56	134.76.	95.141
Pressure in mms. ...	252.13	285.53	320.63	367.20	425.09	596.63
<i>Pv/mT</i> .....	668.09	668.89	665.70	664.14	661.80	655.76

Weight the same. Temperature = 129.6°.

Volume in c.c.s. ....	229.48	202.27	179.80	156.62	134.82	95.182
Pressure in mms. ...	262.05	296.89	323.48	381.97	442.36	620.99
<i>Pv/mT</i> .....	669.32	668.39	667.38	665.85	663.79	657.87

## Sample B. II.

Weight of substance = 0.24181 gram. Temperature = 129.6°.

Volume in c.c.s. ....	229.50	202.29	179.81	95.079
Pressure in mms. ...	283.45	321.13	360.74	671.78
<i>Pv/mT</i> .....	669.00	668.06	666.83	656.88

Compressibility at 129.6°.

Volume .....	32.388	19.386	12.337
Pressure .....	75.893	126.59	198.50
Factor .....	0.27411	0.27411	0.27411
<i>Pv/mT</i> .....	673.49	672.40	671.00

*Pv/mT* from experiments I. and compressibility = 674.40

" " II. " = 674.73

Mean..... = 674.57

## Benzene. Sample A. I.

Weight of substance = 0.26700 gram. Temperature = 129.60°.

Volume in c.cs. ....	179.937	162.09	142.87	126.39	107.05
Pressure in mms. ....	453.44	502.72	569.34	641.99	755.41
Pv/mT .....	789.48	788.49	787.09	785.17	782.52

Weight the same. Temperature = 99.71°.

Volume in c.cs. ....	179.83	162.00	142.79	126.34
Pressure in mms. ....	418.86	464.19	525.46	592.44
Pv/mT .....	787.39	786.10	784.30	782.40

## Sample B. II.

Weight of substance = 0.18606 gram. Temperature = 129.60°.

Volume ...	229.24	202.08	179.63	156.48	134.71	114.69	95.075
Pressure ...	239.35	271.31	304.85	349.22	404.88	474.41	570.09
Pv/mT .....	792.24	791.61	790.64	789.08	787.52	785.64	782.61

Weight the same. Temperature = 99.71°.

Volume ...	229.46	202.25	179.77	156.62	134.83	114.36	96.80
Pressure ...	258.84	293.32	329.62	377.82	438.12	513.50	617.98
Pv/mT .....	793.82	792.92	791.98	790.88	789.52	787.86	785.98

Compressibility at 129.6°.

Volume .....	55.505	29.276	17.532	11.162
Pressure .....	40.047	75.893	126.59	198.50
Factor .....	0.35875	0.35875	0.35875	0.35875
Pv/mT .....	797.44	797.09	796.20	794.88

Pv/mT at zero pressure = 798.1.

## Hexane. Sample A. I.

Weight of substance = 0.29424 grams = m. Temperature = 99.71°.

Volume in c.cs. ....	218.37	198.47	153.86	132.93
Pressure in mms. ....	358.38	393.63	505.15	582.28
Pv/mT .....	714.54	713.30	709.63	706.71

Weight the same. Temperature = 114.90°.

Volume in c.cs. ....	218.47	198.56	153.93	132.99
Pressure in mms. ....	373.27	409.98	526.33	607.21
Pv/mT .....	715.36	714.12	711.81	708.37

Weight the same. Temperature = 129.6°.

Volume in c.cs. ....	239.11	218.56	198.64	175.73	153.99
Pressure in mms. ....	355.02	388.07	426.48	480.98	547.55
Pv/mT .....	717.44	716.83	715.99	714.33	712.63

## Sample A. II.

Weight of substance = 0.19298 gram. Temperature = 129.60°.

Volume in c.cs. ....	229.43	202.22	156.58	134.77	114.78	95.15
Pressure in mms. ...	243.67	276.04	355.54	412.34	483.01	580.73
Pv/mT .....	720.42	719.34	717.37	716.12	714.43	711.93

Weight the same. Temperature = 99.71°.

Volume .....	229.23	202.05	179.59	156.44	134.65	114.68	95.133
Pressure .....	225.37	255.21	286.84	328.59	380.76	445.88	535.54
Pv/mT .....	719.21	717.85	716.97	715.62	713.77	711.67	708.65

Compressibility at 129.60°.

Volume .....	52.472	27.660	16.562	10.540
Pressure .....	40.047	75.893	126.59	193.50
Factor .....	0.3446	0.3446	0.3446	0.3446
Pv/mT .....	724.24	723.51	722.61	721.10



## Normal Octane.

Weight of substance = 0.36007 gram. Temperature = 125.6°.

Volume in c.cs. ....	239.13	198.62	154.04	133.17
Pressure in mms. ....	320.14	383.73	490.78	564.74
Pv/mT .....	534.04	531.68	527.16	524.08

Weight the same. Temperature = 131.4°.

Volume in c.cs. ....	198.90	175.07	153.42	132.55
Pressure in mms. ....	389.24	438.15	498.31	573.26
Pv/mT .....	531.66	529.44	527.66	524.84

## Compressibility.

Volume in c.cs. ....	57.740	30.386	18.155	11.581
Pressure in mms. ...	40.047	75.893	126.59	198.50
Factor .....	0.23514	0.23514	0.23514	0.23514
Pv/mT .....	543.71	542.23	540.40	538.20

Pv/mT at zero pressure = 544.4.

## Di-isobutyl.

Weight of substance = 0.26359 gram. Temperature = 129.60°.

Volume .....	229.27	202.06	179.58	156.40	134.61	94.97
Pressure .....	249.57	282.67	317.53	363.44	420.83	590.45
Pv/mT .....	539.83	538.86	537.97	536.27	534.43	529.03

Weight the same. Temperature = 114.90°.

Volume .....	229.18	201.99	179.53	154.57	94.95
Pressure .....	240.03	271.68	304.94	404.01	565.69
Pv/mT .....	538.68	537.37	536.06	532.39	525.96

## Compressibility.

Volume .....	46.181	24.316	14.539	9.211
Pressure .....	40.047	75.893	126.59	198.50
Factor .....	0.29494	0.29494	0.29494	0.29494

Pv/mT at zero pressure = 546.2.

Inasmuch as the value of this research is absolutely dependent on the purity of the liquids employed it appears necessary to give a rigorous proof of the fact. Mere confirmation of the concordance of any two sets of determinations with the same sample of any one substance would be convincing only as regards the accuracy of the method; it is necessary to prove that, at least in several cases, samples of the same substance, differently prepared or differently treated, yield practically identical results. With the substances kindly furnished by Prof. Young redistillation from phosphoric anhydride was the only means of purification which we could attempt, for we had only small amounts at our disposal; an example of the effect of thus treating normal hexane will be found in the following table. It did not appear obvious how we could improve on a sample of the purest thiophene-free benzene of absolutely constant boiling-point which had been

purified by frequent recrystallization. Nor could we devise another and better way of obtaining a reliable sample of methyl-alcohol than by hydrolysing methyl oxalate, itself prepared from "pure" methyl-alcohol, and drying the resulting alcohol by help of the best lime obtainable. It is true it might have been recrystallized, but as the only likely impurity was water, the handling of the sample would have reintroduced moisture, and the purification would have been an illusory one. We therefore rely on results obtained with ether and with toluene in order to show that the deviation from what may be conveniently termed "theory" is real, and not due to the presence of traces of impurity.

In order that the results of different series of measurements shall be comparable (for the pressures are not the same in any two observations) curves were constructed independently from the observations made with each sample, and the values of  $pv$  at certain definite pressures were read off from these curves, on which the values of  $pv/T$  were plotted on a very open scale. We give first comparative results with two samples of hexane, or rather with two tubes filled at the same time from the same sample; the observations have been made at two temperatures. This serves to show the accuracy of which the method is capable.

#### Hexane.

Temp.	Pressure.	$Pv, mT.$		
		A.	B.	Difference.
129·60°	540	712·90	712·93	0·03=1 part in 24000
	450	715·16	715·20	0·04=1 part in 18000
	390	716·65	716·70	0·05=1 part in 14500
	300	718·93	719·00	0·07=1 part in 10300
99·71°	480	710·42	710·40	0·02=1 part in 35000
	420	712·40	712·42	0·02=1 part in 35000
	360	714·45	714·50	0·05=1 part in 14000
	300	716·46	716·53	0·07=1 part in 10000

The greatest difference between any two measurements is thus 1 part in 10000. With benzene, the results were obtained from two different portions, distilled at different times from the same stock.

## Benzene.

Temp.	Pressure.	Pv/mT.		
		A.	B.	Difference.
129·60°	680	784·34	784·42	0·08=1 part in 9800
	560	787·00	787·10	0·10=1 part in 7900
	440	789·65	789·77	0·12=1 part in 6600
	320	792·32	792·42	0·10=1 part in 8000
99·71°	680	779·58	779·82	0·24=1 part in 3200
	560	783·02	783·28	0·26=1 part in 3000
	440	786·50	786·76	0·26=1 part in 3000
	320	789·96	790·23	0·27=1 part in 3000

Here the limit of accuracy is 1 part in 3000.

The methods of preparation of the three samples of ether have already been mentioned on p. 547. Sample A was distilled from phosphoric anhydride; sample B was left in contact with phosphoric anhydride for some days, and had been shaken with metallic mercury before distillation; while sample C had been recrystallized, and the crystals alone used.

## Ether.

Temp.	Pressure.	Pv/mT.			
		A.	B.	C.	Difference.
129·60°	500	833·70	...	833·78	0·08=1 part in 10000
	400	835·94	...	836·03	0·09=1 part in 9200
	300	838·20	...	838·28	0·08=1 part in 10000
	250	839·36	...	839·43	0·07=1 part in 12000
99·71°	500	830·03	830·25	...	0·22=1 part in 3800
	400	833·03	833·24	...	0·21=1 part in 4000
	300	836·00	836·19	...	0·19=1 part in 4300
	250	837·50	837·68	...	0·18=1 part in 4600

These results show that the ether of all the samples may be regarded as pure. The maximum difference is about part in 4000.

Sample A of toluene was prepared from paratoluidine; sample B from bromobenzene and methyl iodide; sample C was subsequently recrystallized, as described on p. 547.

## Toluene.

Temp.	Pressure.	$Pv/mT$ .		
		A.	B.	Difference.
129.60°	600	658.61	658.93	0.32=1 part in 2000
	480	662.62	662.94	0.32=1 part in 2000
	360	666.43	666.78	0.35=1 part in 1900
	270	669.12	669.36	0.24=1 part in 2800

The greatest difference is observable with toluene; it is probable that the recrystallized sample was purer than the other. But after all, the difference is by no means large enough to affect the conclusions to be drawn.

The next step is to deduce from the measurements given in Table II. the values of  $pv/mT$  at zero pressure, when, if Daniel Berthelot's contention is correct, equal volumes may be expected to contain equal numbers of molecules; a comparison of the true molecular weights should then be possible. The values of  $pv/mT$  were therefore transferred to curves, which are reproduced in Pl. X. : and the curves representing compressibilities, having also been mapped, were shifted in position, so as to become continuous with those in which the true value, and not merely the variation of  $pv/mT$  with pressure, was known. From these two sets of data the complete curves were drawn. The lower limit of pressure lies approximately at from 40 to 60 millimetres.

These curves were extrapolated until they cut the axis of zero pressure. The justice of thus extrapolating the curves will be considered later.

From the weight of a litre of oxygen at 0° C., namely, 1.42961, and from the found coefficient of expansion with temperature, 0.0036694, the molecular weights of the substances employed were calculated, as shown in Table IV.

The absolute value of the molecular weight  $M'$  in each case depends on the coefficient of expansion accepted for oxygen; and this, as has been shown by researches (unpublished) made in the laboratory of University College, varies with the pressure. Were the number 0.003675 to be

TABLE IV.

## Molecular Weights at 129·6°.

$K$  = value of  $Pv/T$  for one gram-molecule of oxygen at 129·6° at zero pressure = 62423.

$K'$  = value of  $Pv/T$  for one gram of substance at 129·6°, and at zero pressure.

$K/K'$  = found molecular weight =  $M'$ .

$M$  = calculated molecular weight on the bases  $O=32$ ,  $C=12$ ,  $H=1\cdot007$ .

Substance.	$K'$ .	$M'=K/K'$ .	$M$ .	Difference 1 part in
Methyl Alcohol .....	194·73	32·056	32·03	1111
Ethyl Ether .....	84·345	74·01	74·07	1250
Hexane .....	72·475	86·13	86·10	2500
Di-isobutyl .....	54·62	114·29	114·13	714
Normal Octane.....	54·44	114·66	114·13	213
Benzene .....	79·81	78·21	78·04	454
Toluene .....	67·44	92·56	92·06	182

accepted instead of 0·36694, the value of  $M'$  for methyl-alcohol would be 32·105, and that for ether 74·12. But such an assumption would have no influence on the main question, viz. the variation in the discrepancies between the values of  $M$  and  $M'$ . From the last column these are seen to vary from 1 part in 1250 (minus) to 1 part in 182 (plus). The discrepancy is made more apparent by accepting for ether the "theoretical" molecular weight; the discrepancy is then :—

Methyl alc.	Ether.	Hexane.	Di-isobutyl.	Norm. Octane.	Benzene.	Toluene.
1 part in 588...	∞	833	455	182	333	159

Now the greatest divergence between results with different samples occurs in the case of toluene; and it is only 1 part in 1900; it is clear, therefore, that the discrepancy cannot be attributed to impurity of material, nor to inaccuracy in experiment. To what cause, then, is it to be ascribed? We have given on p. 545 several hypotheses which may explain the divergence between found and "theoretical" results; these shall now be considered.

First, it is evident that Avogadro's law does not hold for vapours, even under the ideal condition of zero pressure. There would appear to be only three possible causes which would explain the anomaly.

We regard it as unlikely that the volume of the vapour is decreased by the adherence of a film to the glass walls of the volume-tube. It is to be expected that this phenomenon would become more observable at high, than at low, pressures; and one of the authors, in conjunction with Prof. Young, has investigated the behaviour of ether and methyl-alcohol at very high pressures, and Prof. Young has himself examined the hydrocarbons without finding any ground for entertaining this supposition. On the other hand, evidence that it does take place in the case of water has been obtained by them. It is manifested by an apparently continuous, instead of an abrupt, change on passing from the gaseous into the liquid condition. It has an effect in modifying what is often termed the "Andrews" diagram in the same manner as if a permanent gas were present along with the substance under experiment. To quote from the paper mentioned (Phil. Trans. 1892, A, p. 113):—"As the vapour-pressure is approached, the curves, instead of cutting the vapour-pressure line so as to form an angle, as is the case with the other liquids which we have examined, gradually turn and run nearly parallel to the vapour-pressure line at a somewhat lower pressure. When a considerable amount of liquid has condensed the true vapour-pressure is reached." Now this phenomenon increases with rise of pressure; but in the experiments of which an account has been given in this paper, the curvature is such as to show that the rate of increase of  $pv/T$  is less at low than at high pressures. Not merely, then, is the phenomenon absent in the class of liquids under experiment, but even if it should be conceived to be present its variation with pressure is in the wrong direction. We think, therefore, that it may be dismissed from further consideration.

That the formation of complex molecular groups is the cause of the high density of these vapours is certainly a conceivable supposition, but hardly a tenable one. For methyl-alcohol, which is known to consist of complex groupings in the liquid state, exhibits, if ether is taken to possess the theoretical molecular weight, a divergence of only 1 part in 588; whereas the hydrocarbons, which show no such tendency, are characterized by a greater discrepancy, all except hexane.

Another supposition which deserves consideration is that although there may be no molecular groupings, yet the molecules attract one another, and thus lower the value of the product  $Pv$ . And it is conceivable that the nearer the boiling-point of the substance to the temperature of experiment,  $129.6^\circ$ , the more this attraction should manifest itself. This possibility finds support to some extent by the results. The order of divergence does present a general correspondence with the order of boiling-points; but the numbers are reversed between three pairs of substances, as may be seen from the table which follows:—

	Ether	Hexane.	Methyl alc.	Di-iso- butyl.	Benzene.	Octane.	Toluene.
1 part in .....	...	833	588	455	333	182	159
Boiling-pt. ....	$35^\circ$	$69^\circ$	$66^\circ$	$109^\circ$	$80^\circ$	$128^\circ$	$110^\circ$

The boiling-points of methyl-alcohol and hexane, of benzene and di-isobutyl, and of toluene and octane follow the wrong order. Still, if substances belonging to the same class be compared, hexane, di-isobutyl, and octane show correspondence; and so, too, do benzene and toluene.

Another plan of attacking the problem is to compare the values of the expression  $d(Pv)/dP$  for all the substances at certain definite pressures and temperatures, the same for all; in other words, to compare the slopes of the curves with the divergences from the "theoretical" vapour-densities. This is done in the following table:—

	Discrepancy 1 part in	Temp.	Relative values of $d(Pv)/dP$ at the pressures		
			500 mms.	300 mms.	100 mms.
Me. Alc....	588	$130^\circ$	0.000197	0.0000160	0.0000114
Ether ...	...	130	0.0000282	0.0000271	0.0000184
		100	365	347	
Benzene ...	333	130	286	278	208
		100	376	348	
Hexane ...	833	130	379	321	277
		115	422	402	
		100	480	434	
Toluene ...	159	130	466	420	282
		115	548	512	
		100	664		
Di-isob. ...	455	130	623	595	480
		115	740	710	
Octane ...	182	130	720	656	593

It is clear that the order of discrepancy bears no relation to the order of slope at any of the temperatures or pressures.

With a theoretically "perfect" gas, in the ideal state in which its molecules occupy no space and exercise no attraction on one another, the curve representing  $Pv/T$  should run parallel to the pressure-axis. This condition is nearly satisfied by the gases examined by M. Daniel Berthelot, all of which were weighed at temperatures much above their critical points. One would have imagined that at sufficiently low pressures the distance between the molecules of vapours such as those examined would be so great that neither molecular attraction nor the size of the molecules would influence the result; and it might have been expected that the curves showing variation of the value of  $Pv/T$  with pressure should become parallel to the pressure-axis at sufficiently low pressure. It is, of course, possible that at pressures lower than 40 millimetres—the lowest measured—the curves might become parallel. A glance at figure 5 (Pl. X.) will show this. But it is to be noticed that no such change in the slope of the curve in extrapolating to zero pressure would have had any important influence on the discrepancy. We have for all these reasons been unable to establish any connexion between the volatility of the substances examined and their divergence from the "theoretical" molecular weights.

The last supposition, viz., that it is possible that the atomic weights of the elements may depend on the proportion in which they are present in the compounds which contain them, is added only for the sake of completeness. Even if it be considered, there is no regularity in the cases examined which would lend probability to the hypothesis.

It must therefore be concluded that the determination of the density of a vapour does not serve as a means of arriving at a conclusion regarding the accurate atomic weights of the elements present in the compound.

#### DISCUSSION.

Prof. EVERETT referred to the work of Regnault and Amagat upon the variation of the product  $p_v$  at high pressures.



Dr. A. GRIFFITHS, in commenting on the theoretical basis of the comparison of densities, indicated his lack of confidence in one of the fundamental hypotheses, viz., that the temperature of a given gas depends simply on a single factor, the mean square of the linear velocity of the molecules.

Dr. LEHFELDT asked what standard substance had been employed throughout the investigation and whether the authors were satisfied that the different graphs of  $\frac{pv}{T}$  all cut the zero-pressure line in the same point. The experiments seemed to be in agreement with Lord Rayleigh's statement that at low pressures  $\frac{pv}{T}$  is a constant for the permanent gases.

Sir W. RAMSAY said that the standard substance used was oxygen, and that the curves obtained for any vapour at different temperatures practically cut the zero-pressure line at the same point.

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#### LVI. *On Astigmatic Aberration.*

By R. J. SOWTER, *B.Sc., A.R.C.S.\**

THE paper affords a simple explanation for some of the shadow phenomena observed by Prof. S. P. Thompson in his experimental researches on the aberration of lenses†, namely, in those experiments in which the aberration is wholly or in part astigmatic. In investigating the properties of non-homocentric pencils or beams with one or more kinds of aberration present, it is necessary to determine what part is played by each of the several kinds of aberration. It is of interest to know what is the effect of, or part played by, astigmatic aberration in the production of shadows by objects placed in, or moved about in, non-homocentric pencils or beams. It will be found that the presence of astigmatic aberration in a non-homocentric beam is accountable merely for the twist

\* Read December 12, 1902.

† "Some Experiments on the Zonal Aberration of Lenses." *Extrait des Arch. Néerland des Sc.* and Traill Taylor Lecture, 1901. "Shadows in Astigmatic Beams," Prof. S. P. Thompson, *Proc. Phys. Soc.* June 12, 1903.

or rotation shown in the shadow or image formed by an object placed in or moved about in the beam.

To examine mathematically the twists produced in a pure astigmatic non-homocentric pencil or beam, the symmetrical standard pencil, such as is investigated by Heath (*Geometrical Optics*, p. 142), is assumed.

If the axis of the beam is the axis of  $z$ , and the origin is at the intersection of this axis with a selected orthogonal surface or plane cutting the beam in an ellipse of which the axes are  $2\alpha$ ,  $2\beta$ , respectively, the equation to the bounding surface of the beam is

$$\frac{x^2}{\alpha^2\left(1-\frac{z}{f_1}\right)^2} + \frac{y^2}{\beta^2\left(1-\frac{z}{f_2}\right)^2} = 1^*, \dots \quad (1)$$

where  $f_1$  and  $f_2$  are the distances of the focal lines from the selected plane.

If  $\xi$ ,  $\eta$ , are the coordinates of a point in the selected ellipse it is easily shown that

$$\xi = \frac{x}{1-\frac{z}{f_1}} \quad \text{and} \quad \eta = \frac{y}{1-\frac{z}{f_2}},$$

and if the eccentric angle of the point ( $\xi \eta$  0) in the ellipse is  $\phi$  then

$$\xi = \alpha \cos \phi,$$

$$\eta = \beta \sin \phi,$$

and

$$x = \alpha \left(1 - \frac{z}{f_1}\right) \cos \phi,$$

$$y = \beta \left(1 - \frac{z}{f_2}\right) \sin \phi.$$

So that if  $\theta$  is the inclination of the radius to the point  $x y z$

$$\tan \theta = \frac{\beta}{\alpha} \cdot \frac{\left(1 - \frac{z}{f_2}\right)}{\left(1 - \frac{z}{f_1}\right)} \cdot \tan \phi.$$

\* Heath, *Geom. Optics*, § 142, p. 161.

One section of the beam being assumed elliptical it follows from the equation (1) of the bounding surface that all sections of the beam are elliptical, the circular sections being particular forms.

Let the lengths of the primary and secondary focal lines be  $2a$  and  $2b$  respectively, and let the focal interval be  $\delta$ .

The equation to the bounding surface of the beam, the origin being transferred to the middle point of the primary focal line, can be expressed as

$$a^2(\delta - z)^2(\delta^2 y^2 - b^2 z^2) + b^2 \delta^2 x^2 z^2 = 0.$$

This equation is the equation of the skew surface generated by the movement of a variable ellipse between the focal lines, the axes of the generating ellipses remaining parallel to the focal lines.

Through any point  $(xyz)$  on this skew surface there is one generator or ray, viz.:—

$$x = \frac{a \cos \phi}{\delta} (\delta - z)$$

$$y = \frac{b \sin \phi}{\delta} (z).$$

This ray intercepts the primary and secondary focal lines at distances from the axis of the beam of  $a \cos \phi$  and  $b \sin \phi$  respectively.

If  $\theta$  is the inclination of the radius to the point  $xyz$

$$\tan \theta = \frac{bz}{a(\delta - z)} \cdot \tan \phi.$$

Any ray or generator of the astigmatic surface has for its equation

$$\phi = \text{constant} = \tan^{-1} \frac{a \epsilon}{b \gamma},$$

where  $\gamma$  and  $\epsilon$  are the intercepts of the ray or generator on the focal lines, the intercepts being measured from the axis of the beam.

This simple formula  $\phi = \text{constant}$  expresses in a most convenient form the general equation for any ray of a symmetrical astigmatic beam, and exemplifies for such a ray the



since  $\phi_1 = \tan^{-1} \frac{a e}{b \gamma}$ , and  $\phi_1$  is the eccentric angle of the point  $i$  in the ellipse on the receiving screen.

A small point-like object placed in the beam at  $P$  will cast a small point-like shadow on the screen, and the shadow with the positions taken will be inverted in respect to top and bottom, and will be unchanged in respect to side and side.

A straight wire placed say at  $45^\circ$  across the beam and cutting the axis of the beam will depict on the screen a straight-line shadow in the ellipse on the screen, and this shadow is at a definite inclination. The inclination depends on the relative distances and positions.

If the wire is considered to intercept the bounding surface of the beam in a point, the eccentric angle of which is  $\phi$ , the line shadow in the ellipse on the screen is at an inclination defined by the eccentric angle  $\phi$ .

Generally, if the wire is inclined at  $\theta$  and is at a distance  $z$  from the primary focal line, the value of  $\phi$  is obtained from the equation

$$\tan \theta = \frac{b z}{a(\delta - z)} \tan \phi.$$

If an inclined straight wire is placed across the pencil or beam and is moved, without varying its inclination, from the primary focal line to the secondary focal line, the shadow rotates through an angle of  $\frac{\pi}{2}$ , for  $\phi$  changes by  $\frac{\pi}{2}$  in passing from one focal line to the other.

In non-homocentric pencils or beams that are not purely astigmatic but are compounded of astigmatic and other aberrations, the presence of astigmatism shows itself in or is accountable for the twists or rotations that are discernible in the shadows or images formed by objects placed in or moved about in such pencils or beams.

For instance, if in the experimental pencil or beam there are astigmatic and spherical aberrations present, then a straight wire placed across the beam and moved about does not cast a straight-line shadow, but casts a distorted shadow, such as a figure of  $S$ , which is displaced through an angle or is rotated, the displacement or rotation being due to the astigmatic aberration present in the beam.

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## DISCUSSION.

Prof. EVERETT asked if the paper dealt with a zone or with the whole of a pencil. He said that generally the focal lines were not at right angles. In the case of an ordinary lens at  $45^\circ$  to the axis of a pencil, the cross sections of the secondary focal region for a narrow zone of the lens were figures of 8, and the true secondary line was the locus of the point of self-cutting of the 8. It was nearer to parallelism with the axis than to perpendicularity. The cross sections of the primary focal region were curves with two points of self-cutting.

Dr. R. T. GLAZEBROOK said, in reply to Prof. Everett's observation, that much of the author's work was based on the assumption that the focal lines were at right angles. The analysis had been simplified by the author by assuming that the surface can be generated by the motion of an ellipse, but he thought this assumption ought to be justified. He showed how the results arrived at in the paper could be obtained more generally without any such assumption, basing his proof on formulæ given in Heath's 'Optics,' p. 161.

Mr. PRICE referred to a figure similar to the elliptic trammels. An infinite bar moves so that two determined points upon it move along two fixed straight lines which are not coplanar and need not be at right angles. Every other point on the bar moves in a curve of the second degree in a plane parallel to the two fixed lines. If the two fixed straight lines are at right angles, the central point of the bar describes a circle, and if the motion of this point be uniform, that of every other point is harmonic. The surface described by this infinite bar is similar in character to that of an astigmatic pencil, being like a double cone, whose generators are straight, and all pass through two straight lines which do not intersect.

The AUTHOR, in reply, said that he had made certain assumptions to give a simple explanation of the shadow phenomena observed by Prof. Thompson. The fact that a generator of the surface could be expressed by the equation  $\phi = \text{constant}$  rendered this explanation easy. With reference to Prof. Everett's question, he said that the analysis applied to the bounding surface of an astigmatic beam.

LVII. *On the Interpretation of Milne Seismograms.*

By C. COLERIDGE FARR, D.Sc.\*

[Plate XI.]

THE question whether a horizontal pendulum Seismograph acts as a clinograph or whether its records must in part be ascribed to horizontal movements of the Earth's surface has received discussion by Milne†, Omori‡, and by others also whose arguments I have not been able to peruse. Both Prof. Milne and Dr. Omori conclude that the tilts represented by the maximum displacement of the boom would indicate earth movements too large to be admissible.

Without attempting to give a complete theory§ of the movement of the boom, or denying that horizontal movements may occur when the inertia weight will act as a steady point, yet from the ordinary elementary theory of forced vibrations|| the equation giving the movement of a vibrating body, whose "free" frequency is  $n/2\pi$ , under the action of a periodic force  $E \cos pt$ , is

$$u = \frac{E}{\sqrt{(n^2 - p^2)^2 + k^2 p^2}} \cos (pt - \epsilon). \quad (1)$$

If  $k$ , the resistance due to friction, be small compared with the difference of the squares of the frequencies, the resulting vibration has an amplitude

$$u = \frac{E}{n^2 - p^2}, \quad (2)$$

whilst, as is well known, the period of the vibration takes the period of the disturbing cause.

Though an earthquake record is probably due to several terms of the form  $E \cos pt$  with different coefficients of decay,

\* Read March 13, 1903.

† 'Nature,' vol. lxx. p. 202, and B. A. Report Seismological Committee.

‡ Publications of the Earthquakes Investigation Committee, No. 5, Tokyo, 1901, p. 45, *et seq.*

§ The theory of the horizontal pendulum is discussed at length in *Comptes Rendus des Séances de la Commission Seismique Permanent 1902*, which reached me after this paper was written.

|| Rayleigh, 'Sound,' 1st ed. vol. i. p. 38.

yet in many instances I have seen a considerable portion of the record appear to consist of waves of one wave-length, in which case the above simple formula will give at least a general idea of the earth movement corresponding to any diagram; but to obtain it a knowledge of " $p$ " as well as " $n$ " is necessary, for which purpose the tape must be driven sufficiently fast for the period of the forced vibration to be determined, which is not the case with Milne seismographs as at present constructed.

A possibility in these diagrams which appears to have been overlooked is that of interference effects between the forced and free vibrations of the boom. In order to ascertain the effect of periodically loading the pillar, I attached wooden boxes on its east and west sides. These were filled with sawdust. Two chains, fastened together by a rope passing over two pulleys fixed to the ceiling, were hung one over the centre of each box, and the rope was of such a length that the chains just touched the sawdust in the boxes together. By working this arrangement up and down at definite speed, I was able to imitate in a rough way a periodic tilting of the pillar. The total movement of the boom when one chain was removed from its box and the other placed in its proper box was 1.6 mm., i.e. the tilt was  $\cdot 35''$  whilst the chain was in its box. With this apparatus I imitated in succession waves of periods of 12, 13 ... to 20 seconds, whilst the boom period was 16.5 seconds throughout. I had previously increased the tape speed sufficiently to be able to count the number of vibrations of the boom. Some of the diagrams thus obtained are reproduced (figs. 1 to 4, Plate XI.). In every case the number of vibrations performed by the boom was exactly the same as the number of motions of the chain. In every case also the amplitude due to periodic displacement was greater than that due to steady loading, though in no case did the simple formula (2) give the observed extent of the swing. The latter is always less than it should be. The discrepancy is probably due to three causes: (1) The imperfect representation of a sine curve with the apparatus. (2) It does not follow (as indeed it is one of the objects of this paper to point out) that because the pillar was tilted  $\cdot 35''$  when statically loaded, that it was also tilted that amount when periodically loaded by the same



weight—it depends on whether  $n^2 - p^2$  as applied to the pillar was  $> =$  or  $< 1$ . (3) A certain amount of viscosity exists in the pillar, which prevents it responding promptly to its load.

The diagrams show interference effects well, especially that representing 15 sec. waves. That some of the throbbings so common in earthquake diagrams from the Milne instrument, and called by Professor Milne "Echoes"\*, are in reality interference effects I have little doubt. The 15 sec. diagram shows a series of lens-shaped throbbings remarkably like a very common feature of a seismogram. The interval given by Milne of usually from 2 to 6 minutes† between the shock and its echo is exactly that between the beats. On the 15 sec. diagram the interval is about three minutes for a boom period 16.5. With a nearer approach to isochronism the interval would be longer until, if the periods are sufficiently near, the free vibration will have been damped out before opposition in phase can occur. This is evident in the 16 sec., 17 sec., and 18 sec. diagrams.

The object of this paper is to point out that on ordinary elementary theory it is erroneous to derive information regarding the movement of the earth from the measurement of the boom of a Milne seismograph as at present constructed, as we have no knowledge to what extent synchronism may affect the result. To obtain the necessary knowledge the tape must be driven at a higher speed, or it might be obtained in some cases from the interference effects. In cases where there is a near approach to isochronism between the boom period and the wave period, the amplitude of swing depends largely on the damping effect of friction (equation 1), which is entirely ignored at present in this connexion.

#### DISCUSSION.

Dr. R. T. GLAZEBROOK said the paper brought out clearly the possibility of interference between the periods of the boom and the earthquake tremors.

Prof. PERRY said that, if possible, the period of the pendulum should be very different to that of the wave. The

\* British Association Reports, p. 227 (1899).

† British Association Reports, p. 72 (1900).

period might be made very great or excessively small, but there would probably be difficulties in either case.

Prof. EVERETT said it was obvious that the records could not easily be interpreted unless there was a great difference between the periods. He suggested the use of two booms having different periods.

Dr. WATSON pointed out that the boom would respond equally well to any period if it was heavily damped. Fluid damping was unsatisfactory because of convection currents, and he suggested that the plate at the end of the boom should be made of copper and allowed to move between the poles of a strong horse-shoe magnet.

Dr. CHREE said that if the period of the boom was increased beyond 18 seconds, the apparatus became too sensitive and was unstable.

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LVIII. *On an Instrument for Measuring the Lateral Contraction of Tie-bars, and on the Determination of Poisson's Ratio.* By J. MORROW, M.Sc. (Vict.), Lecturer in Engineering, University College, Bristol\*.

THE ratio of the lateral to the longitudinal strain in a bar under the action of a simple pull or push in the direction of its axis has been the subject of much controversy and a considerable amount of research. Some French mathematicians, including Poisson and Navier, held that this ratio was  $\frac{1}{4}$  for all isotropic substances, their arguments were based on a theory of the constancy of the ratio of the elastic coefficients for all materials.

Wertheim endeavoured to show that this theory was false. He filled hollow prisms with liquid and subjected them to a tensile force. The interior of the prism communicated with a capillary tube, and the change of volume of the interior was measured by the distance the fluid advanced or receded in the tube. If Poisson's ratio be denoted by  $\sigma$ , change of unit volume = tensile strain  $(1 - 2\sigma)$  very approximately. He maintained that the ratio  $\sigma$  should really be

\* Read May 22, 1903.

$\frac{1}{3}$  for all materials; but it appears doubtful whether the specimens dealt with were sufficiently isotropic to justify any definite conclusion either for or against the uniconstant form.

Practical methods for the determination of Poisson's ratio may be divided into three classes. First, those by which two coefficients of elasticity are obtained, and the required ratio inferred by calculation. Second, those which depend on the deformation of the section of a beam when bent. And, lastly, methods by which the tensile and lateral strains are actually measured in specimens of the material under direct tensile or compressive stress.

Kirchhoff experimented in 1859 upon cylinders, which by means of a weight attached to a lever were put simultaneously under the action of bending and twisting forces and the strains produced were measured accurately. The values of Poisson's ratio were calculated from the ratio of the observed displacements, and were

Mean for three steel rods . . . .	·294.
„ hard drawn brass rod . . .	·387.

Many others have worked on similar lines.

Cornu (and later Straubel) explored the anticlastic surface of a rectangular beam by means of the interference-fringes produced between it and a plate of glass laid on it, thus obtaining data for the calculation of  $\sigma$ .

Mallock (1879) also examined the anticlastic curvature. By means of a microscope he measured the movement of four fine steel wires fastened to opposite diameters of a circle on the surface, obtaining data for the radii.

Another method of investigation would be to find the displacements in the sides of a beam, either by measuring the lateral strains at any section, or by attaching a mirror to the side and finding the angle through which it turns when the beam is loaded.

If  $f$  = the maximum tensile stress, the lateral contraction is  $\sigma \frac{f}{E} b$  ( $b$  being the breadth of the beam and  $E$  Young's modulus) and the angle turned through by the side of the beam is  $\tan^{-1} \sigma \frac{f}{E} \frac{b}{a}$ .

In all the above methods the practical accuracy of the theory of elastic materials is assumed.

Coming now to actual measurements of the lateral contraction of a tie-bar, it appears that Bauschinger (*Der Civilingenieur*, vol. xxv. 1879, pp. 81-124) was the first to construct an instrument which would measure the alteration of cross dimensions of a metal test-piece. His apparatus is complicated. It is essentially a pair of levers, the small arms of which are the diameter of small caoutchouc cylinders, and the greater the double distance of the scale from a mirror. To read the lateral contraction requires two separate observations by means of two telescopes and mirrors on opposite sides of the specimen.

Stromeyer (Proc. Roy. Soc. vol. lv. no. 334, p. 373) measured directly the lateral contraction of a bar under tension by interference methods; a dark glass attached to the specimen advanced or receded from the surface of a prism as the diameter of the specimen altered, thus producing change in the positions of the interference-bands.

#### *Elastic Constants.*

If  $\alpha$  is the longitudinal strain produced by unit stress, and  $\beta$  the linear lateral strain in the material, then

$$\sigma = \frac{\beta}{\alpha}, \quad E = \frac{1}{\alpha}, \quad n = \frac{1}{2(\alpha + \beta)}, \quad \text{and} \quad k = \frac{1}{3(\alpha - 2\beta)};$$

where  $E$ ,  $n$ , and  $k$  are Young's modulus and the moduli of rigidity and of bulk respectively.

If any two of the elastic coefficients be known Poisson's ratio can be calculated.

Also we have that:—

if  $\sigma = \frac{1}{2}$  the material is incompressible, and the extension and lateral contraction are such that the volume remains constant.

if  $\sigma > \frac{1}{2}$   $k$  would be opposite in sign to  $E$  and  $n$ , the material not being homogeneous and isotropic.

if  $\sigma = 0$  to  $\frac{1}{2}$  we have an ordinary elastic body.

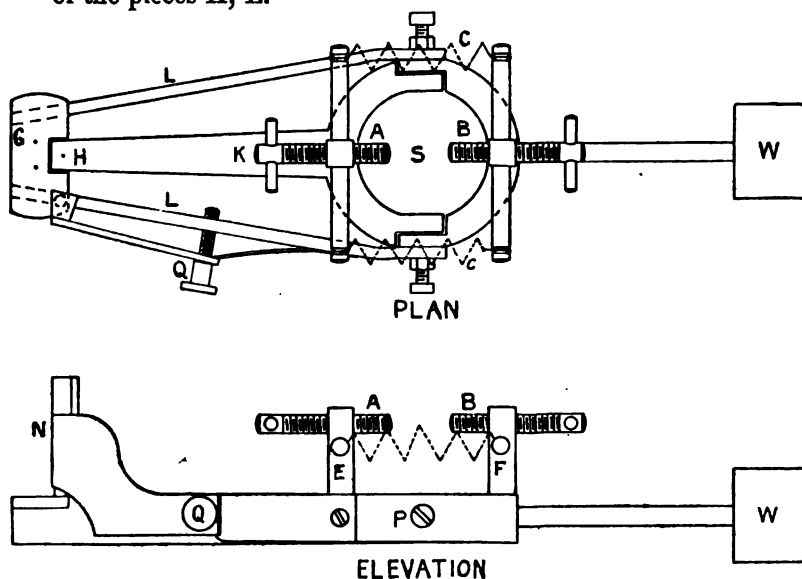
if  $\sigma = 0$  either there is no lateral strain or the material is perfectly plastic.

$\sigma = \frac{1}{2}$  is the value of the uniconstant theory which requires  $n = \frac{2}{3}$   $k = \frac{2}{3}$   $E$ .

*The New Form of Apparatus.*

With the object of measuring, in the most direct way possible, the lateral contraction of a tensile specimen or the dilatation of a compressive piece when loaded in an ordinary testing-machine, the author devised the instrument shown in the figure.

Two hardened set-screws A and B, on opposite sides of the specimen S, are pressed inwards by stiff springs C, C. The relative motion of the points of these set-screws is transmitted by the bars E, F, and the pivot P, to the extremities H, G, of the pieces K, L.



SCALE HALF SIZE

It will be noticed that the instrument touches the specimen only at the points between which the alteration of dimension is to be measured. When the specimen extends A and B approach one another, and consequently G falls with reference to H. The relative displacement of G and H is measured optically. A mirror M rests by three steel points (two of which are on G and the other on H, as shown in the plan of the instrument) on glass plates fixed to G and H. A second mirror N is attached to G in a vertical position, it

is capable of a small amount of rotation about a vertical axis by the fine adjustment screw Q. The two mirrors are close together but not touching. A scale is placed some distance away, and by means of a telescope two images of the scale are seen, one in each mirror. These images are brought together in the telescope and the one is read against the other. Thus a certain convenient reading on the N image is taken as the index, and as the load is applied to the specimen the observer reads the values on the M image coinciding with this index.

Every precaution has been taken to ensure the greatest possible accuracy. The screws A and B have spherical points in order that they may not cut into the specimen. The instrument is balanced by the weight W. The mirrors are of specially worked optically plane glass. The joint at P is made by centring the screws in the inner piece, and is constructed with the greatest care.

In order to test the instrument a specially selected bar of mild Bessemer steel was used. It was turned to one inch diameter as given by a Whitworth gauge. After placing in the testing-machine it was loaded several times up to 5 tons. The instrument was attached and allowed to stand for a short time before readings were taken.

The load was then applied by successive tons between the limits 1 and 5 tons and the scale-readings observed. The results for three series of increasing and decreasing loads are given in Table I.

It was thus seen that the readings could be repeated with considerable accuracy. The above are some of the first readings taken, further experience in the use of the instrument led to still more uniform results.

#### *Experimental Determination of Poisson's Ratio.*

In these experiments the load on the specimen was in some cases varied from 1 to 5 tons, and in others from 1 to 3 tons. In the former the readings were taken at intervals of 1 ton, and in the latter at intervals of one-half ton. In every case the specimens were loaded several times previous to the readings being taken. In order to insure complete immunity from local strains (due to the method of gripping the specimen)

TABLE I.

Load.	Scale-Readings.			Differences.		
	1st Loading.	2nd Loading.	3rd Loading.	1st Loading.	2nd Loading.	3rd Loading.
1	195.0	201.2	201.8			
2	197.9	204.0	204.7	2.9	2.8	2.9
3	200.7	206.9	207.6	2.8	2.9	2.9
4	203.6	209.8	210.4	2.9	2.9	2.8
5	206.1	212.6	213.2	2.5	2.8	2.8
4	208.4	210.0	210.7	2.7	2.6	2.5
3	200.5	207.4	207.9	2.9	2.6	2.8
2	197.7	204.6	205.1	2.8	2.8	2.8
1	194.8	201.8	202.2	2.9	2.8	2.9
Mean diff. per ton ...				2.80	2.78	2.80

an unusually large distance was allowed between the ends of the specimen and the portion of it under observation.

The instrument used was carefully measured under a reading microscope and found to give a magnification of 4.106. The distance between the needle-points of the tilting mirror, measured in the same way, was .2960 in. The normal distance from the mirrors to the line through the scale parallel to the tilting mirror was measured several times in different ways and the mean value taken as correct.

Under these circumstances the total magnification obtained was about 2800, but the exact value of course varied with the position of the telescope and scale.

Table II. contains the results of experiments on specimens of various materials.

The extensions and lateral contractions were measured simultaneously, an extensometer having been specially arranged so that both instruments could be attached to the specimen at the same time and used throughout the experiment.

The calculated means of the observed tensile and lateral strains for half-ton of load are given in the table, and the values of the modulus of elasticity and Poisson's ratio are obtained from these. The modulus is given in lbs. weight

TABLE II.

Material.	Strains per $\frac{1}{2}$ ton of Load.		Young's Modulus.	Poisson's Ratio.	
	Tensile.	Lateral.			
Mild Steel.	·000,0464	·000,0128	30·75 $\times 10^6$	·276	
	·000,0469	·000,0130	30·46	·277	
	·000,0465	·000,0127	30·70	·273	
Sheffield Spindle Steel.	·000,0488	·000,0135	29·60	·277	
	·000,0505	·000,0142	28·33	·281	
	·000,0488	·000,0132	29·23	·271	
Wrought Iron.	·000,0531	·000,0144	29·08	·271	Dia. = ·761 „ = ·707
	·000,0626	·000,0239	29·80	·269	
	·000,0928	·000,0251	30·73	·270	
Drawn Brass (Muntz Metal).	·000,1047	·000,0335	13·26	·320	
	·000,0978	·000,0345	14·23	·353	
	·000,0960	·000,0337	13·61	·351	
Drawn Copper.	·000,0770	·000,0262	17·61	·340	
	·000,0726	·000,0241	18·70	·332	
	·000,0822	·000,0255	16·88	·310	

per sq. inch. It can be expressed in grammes weight per sq. cm. by multiplying the numbers in the table by 70·31.

The specimens were not annealed, and all the above were approximately one inch in diameter except in the cases noted in the table.

*Cast Iron.*—Two sets of cast iron specimens were carefully cast in a vertical position. The first was from a mixture of about equal parts of No. 1 Govan, No. 2 Govan, and Heavy Scrap, and the second from 3 parts Redcar Middlesborough, and one part Scrap.

The material was therefore in each case such as might be used for engine and machine castings.

The specimens were brought to a state of ease by continued application and removal of load until permanent set was completely eliminated.

The values given in Table III. are those obtained from the elastic state of the bar, that is, the strains do not include permanent set.



TABLE III.—Cast Iron.

Specimen.	Diameter.	Strains per $\frac{1}{2}$ ton of Load.		Young's Modulus.	Ratio, $\frac{\beta}{\alpha}$ .
		Tensile.	Lateral.		
1st Series.					
No. 1	·752	·000,1552	·000,0374	$16\cdot25 \times 10^4$	·241
No. 2	1·025	·000,0904	·000,0206	15·01	·228
No. 3	·752	·000,1556	·000,0420	16·21	·270
2nd Series.					
No. 1	·997	·000,0877	·000,0223	16·36	·254
No. 2	·990	·000,0947	·000,0245	15·37	·259
No. 3	·993	·000,0900	·000,0220	16·07	·244

A long series of observations was made for the purpose of determining whether there was any permanent set in the lateral strain. Readings were taken for loads varying by 0·1 of a ton up to 0·5 ton on a C.I. bar approximately 1 inch in diameter. The readings were in  $\frac{1}{40}$  of an inch, and an estimation of  $\frac{1}{10}$  of these was made. The total magnification was 2700. The bar had not been previously loaded, and it appeared to be perfectly elastic as regards lateral strain. On increasing the load up to 1·0 ton, however, there appeared to be a small amount of permanent set, and

TABLE IV.

Material.	Value of Poisson's Ratio.		
	Bauschinger.	Stromeyer.	From Table II.
Mild Steel.....	·29	·273 to ·300	·271 to ·281
Wrought Iron ...	·26 to ·31	·279 to ·301	·270 to ·289
Brass Rod.....	.....	·283 to ·357	·320 to ·351
Copper Rod .....	.....	·325	·310 to ·340
Cast Iron .....	·16 to ·19 (Tension) ·32 to ·38 (Compression)	·148 to ·269	·228 to ·270

between 1.0 and 1.5 tons the set was very marked. It increased in amount up to 3 tons, which was the limit of load applied.

Table IV. is a comparison of the results of other experimenters with those given in this paper.

In conclusion I must acknowledge my indebtedness to my colleague, Mr. E. L. Watkin, M.A., for his valuable assistance in carrying out these experiments, which were made in the Engineering Laboratory at University College, Bristol.

### DISCUSSION.

Prof. EVERETT said he had made determinations of Poisson's ratio by comparing the twist produced in a cylindrical rod by a torque, with the bend produced by an equal torque. The twist was always greater than the bend and the ratio diminished by unity was Poisson's ratio, the material being supposed isotropic. This method was inapplicable to fibrous material: for instance, with wooden rods he had found the twist to be about five times the bend. Mr. Morrow's method had the advantage of being direct, and could be applied to fibrous materials as well as to those which were isotropic. The experiments described in the paper were also on a far larger scale than had heretofore been employed. The mode of attachment of the mirror, which was a point of great importance in the experimental arrangements, seemed to be quite satisfactory.

Dr. CHREE indicated several differences between the author's terminology and that usual in mathematical text-books. He also pointed out the expediency of explaining the units in which the values obtained for Young's modulus were expressed, and of adding the equivalent values in grammes weight per square centimetre. He referred to the fact that in the discussion of Wertheim's experiments on the value of Poisson's ratio given in Todhunter & Pearson's *History of Elasticity*, it was pointed out that the materials employed seemed hardly to be isotropic, and that if this were the case the experiments could not be regarded as decisive. He also pointed out that more than one experimentalist had

obtained results for cast iron which indicated that whilst it might be elastic, in the sense that strain disappeared on the removal of stress, it did not obey Hooke's law; and that if this were the case the application of the term Poisson's ratio to the material was not in accordance with mathematical usage. He dwelt on the importance of corroborative evidence in all cases that the materials dealt with were really elastic and isotropic.

Dr. R. T. GLAZEBROOK said it was difficult to assure oneself that the materials used were isotropic. The author's figures showed different values for Young's modulus for different specimens of the same material. He referred to the importance of stating the units employed, and to the fact that experiments had been carried out on an engineering scale.

Mr. MORROW said the units used in the paper were lbs. and inches. His instrument was not dependent on the ordinary theory of elasticity. He pointed out that the values obtained for the Young's modulus of cast iron depended upon the method employed, elongation and bending giving different results for the same specimen.

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LIX. *Single-Piece Lenses.* By THOMAS H. BLAKESLEY\*.

[Plate XII.]

If the definition of a lens is taken to be a mass of refracting material contained between two spherical surfaces, then any lens is completely determined in shape and size when the radii of curvature of its two end surfaces and the distance between them are given. The dimensions which are measured at right angles to the axis do not affect the focussing properties of the lens except in the second order of small quantities, and such dimensions are not brought into consideration in what follows.

If the kind of material in reference to any kind of light, as defined by the index of refraction of the material for that

\* Read May 22, 1903.

light ( $\mu$ ) is supposed given, there remain only the three linear matters, viz. the two radii of curvature of the surfaces and the distance between the surfaces.

Let these be symbolized under the letters  $r_1$ ,  $r_2$ , and  $d$ .

The third may be considered as always positive, and as to the radii, let them be considered as having a positive value when the light encounters the surfaces upon the concave side; in other words, if the light as it passes generally along the axis passes the centre of a surface *before* it encounters the surface itself.

The variables  $r_1$ ,  $r_2$ , and  $d$  being three in number may then be looked upon as sufficient to determine all the properties relating to focussing for small central pencils of light.

If we contemplate the relations  $\frac{r_1}{d}$ ,  $\frac{r_2}{d}$ , and symbolize them under the letters  $x$  and  $y$ , or, in other words, if we consider  $d$  as unity, we reduce the variables to two in number, and can then represent all the ordinary properties of lenses under a simple system of coordinates, where  $x$  implies the relation of the radius of the first surface to the thickness or length of the lens, and  $y$  a similar magnitude applying to the second surface.

The first diagram (Pl. XII.) is based upon this principle. If we take any point upon the paper its position will indicate some particular lens, and all lenses having some one the same property will lie upon a line drawn upon the diagram. If two such lines meet the point of intersection will correspond to a lens having the properties appertaining to both the lines. The general characters of a lens depend upon its shape and not upon its scale. But if the general characters of a lens are known, and the point on the diagram determined, the strength of a lens is then simply dependent upon the scale, and can be raised as desired.

The diagram presented is based upon the supposition that  $\mu=1.5$ , a supposition which, though it was long employed for glass as sufficiently exact for academical approximation in the casual text-books of Cambridge University, when it was certainly not so, has, under the laborious care of German experiment, become not inapplicable to the glasses of low dispersion produced by Schott.

It may make the use of such a diagram simpler to take an example or two.

Suppose the condition which it is desired to obtain to be that the second principal focus shall lie upon the second surface.

Then from any table of optical properties, *e. g.* that given of lens quantities in my 'Geometrical Optics,' this condition implies that the following equation must hold good:—

$$\overline{\mu-1} d + \mu r_1 = 0.$$

Hence

$$\frac{r_1}{d} = -\frac{\mu-1}{\mu},$$

or if  $\mu = 1.5$ , 
$$x = -\frac{1}{3}.$$

The line is therefore drawn parallel to the axis of  $y$  and at a distance  $-\frac{1}{3}$  from it.

The condition that the focal length shall be infinite is

$$\frac{\mu-1}{\mu} d = r_2 - r_1.$$

Hence  $y - x = \frac{\mu-1}{\mu}$ , or  $\frac{1}{3}$  if  $\mu = 1.5$ .

This straight line is shown upon the diagram and is called the "Telescope Line."

The condition that the focal length shall not change for small variations in the value of the index is of course found by forming the equation  $\frac{df}{d\mu} = 0$ .

This condition is given by the equation

$$\frac{\mu^2-1}{\mu^2} \cdot d = r_2 - r_1.$$

Hence

$$y - x = \frac{\mu^2-1}{\mu^2}, \text{ or } \frac{5}{9} \text{ if } \mu = 1.5.$$

This line is marked "Focal Length a minimum," and is of course parallel to the Telescope Line. All lenses upon this line possess a high degree of achromatism.

A ray may so pass through a lens that it encounters the

two surfaces in such a way as to receive equal deviation in the same direction at each surface, and therefore on the whole minimum deviation, as in the symmetrical passage of a ray through a prism. I have shown elsewhere how this can take place for all the rays of a pencil emanating from any point on the axis of a lens.

If the point is at an infinite distance the condition is

$$\overline{2-\mu} r_2 + \mu r_1 + \overline{\mu-1} d = 0.$$

Hence

$$\overline{2-\mu} y + \mu x + \overline{\mu-1} = 0,$$

and if  $\mu = 1.5$  this becomes

$$y + 3x + 1 = 0.$$

The line is marked upon the diagram "minimum deviation for rays from infinity."

It passes through the sphere point  $x = -\frac{1}{3}, y = \frac{1}{3}$  as all such lines must.

The curve which results from making the position of the second principal focus invariable for a small change in the index is marked  $\frac{dv_0}{d\mu} = 0$ .

It is an hyperbola whose asymptotes make an angle of  $45^\circ$  one with the other. One of these asymptotes is the straight line already considered marked "Focal Length a minimum."

The curves obtainable from such conditions as  $f = n.d.$  i. e. for lenses in which the focal length has a specified relation to  $d$ , are rectangular hyperbolas whose major axis is the line

$$y + x = 0.$$

The numbers corresponding to  $n$  are marked along this line. The points are the centres of the corresponding hyperbolas.

The semiaxes of these hyperbolas are given by the expression

$$\sqrt{\frac{2n+3n^2}{6}}.$$

The second diagram (Pl. XII.) shows the shapes and the

general optical properties of certain lenses which have been constructed on these principles.

The conditions selected are described above, and the relations of the radii of curvature and the focal length to the thickness below, each lens.

The uniform scales indicated along, above, and below the axes give the magnification values for any point, the upper scale for light before, the lower for light after, passage through the lens.

It should also be mentioned that the value of  $\mu$  selected for the computation of the actual quantities was not always 1.5, but depended upon the glass selected.

The first, third, and fourth make very good eyepieces, especially the first, which has all the advantages of a Huyghens' eyepiece, to which it bears a close analogy in its ruling conditions.

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LX. *Radioactive Processes.* By Prof. E. RUTHERFORD.\*

[Abstract.]

THERE are three distinct types of radiation spontaneously emitted from radioactive bodies, which may be called the  $\alpha$ ,  $\beta$ , and  $\gamma$  rays. The  $\alpha$  rays are prominent in causing the conductivity of a gas, they are easily absorbed by metals and are projected bodies, not waves. These bodies are about the size of a hydrogen atom, they are positively charged and travel with about one-tenth of the velocity of light. The  $\beta$  rays are similar in all respects to the cathode rays produced in a vacuum-tube. The  $\gamma$  rays are probably like Röntgen rays, but of very great penetrating power. The  $\alpha$  rays are by far the most important.

In addition to these rays two of the radio-elements give off radioactive "emanations," which are in all respects like gases. The radiations from these emanations are not permanent, but fall off in a geometrical progression with the time. The

\* Read June 5, 1903.

radiation of the thorium emanation falls to half value in one minute, that from radium in four days. They have all the properties of gaseous matter in infinitesimal quantity. Their coefficients of diffusion can be measured, the order of their molecular weights is 100, they are occluded by solid compounds producing them and may be condensed at low temperatures. The radium emanation condenses sharply at  $-150^{\circ}\text{C.}$ , the thorium emanation between  $-120^{\circ}\text{C.}$  and  $-150^{\circ}\text{C.}$  The two emanations excite on objects, with which they come in contact, two kinds of temporary radioactivity, that from the radium emanation decaying much faster than that from the thorium emanation. The latter decays in a G.P. with the time, falling to half value in eleven hours. These effects appear to be produced by solid matter in invisible and unweighable quantity, which can be dissolved off in some acids but not in others. On evaporating the solutions, the radioactivity is obtained unchanged in the residue.

The experiments of Crookes and Becquerel in separating by chemical treatment the matter responsible for the activity of uranium, called uranium X, were referred to, together with the latter's observation that the separated activity had completely decayed after the lapse of a year, by which time the uranium itself had completely recovered its activity.

The work of Rutherford and Soddy on thorium was then discussed in detail. Thorium precipitated in solution by ammonia retains only 25 per cent. of its activity. If the solution is evaporated and ignited the remaining 75 per cent. is found in the extremely small residue left, which, by reason of its separation, is different chemically from thorium and was called Thorium X. Left to themselves, the thorium gradually recovers its activity and the ThX loses it. The activity of the latter falls in a G.P. with the time, the half value being reached after four days. At any time the sum-total of the two activities is a constant. This would occur if the ThX were being continually produced by the thorium, and this was shown to be the case by precipitating thorium at definite intervals after its separation from ThX. The ThX, and not thorium, produces the thorium emanation. The production of ThX by thorium, of the emanation by ThX,



and of the matter causing the excited activity by the emanation, are all changes of the same type, although the rates of change are distinct in each case. The change of uranium into uranium X is also similar, being the slowest of all. Twenty-two days elapse before uranium freed from UrX recovers one half of its activity. In radium the radium emanation is the first product produced, and since this in a solid is almost completely occluded, the activity of a radium salt after it has been obtained from its solution rises after precipitation to several times its original value, due to the occlusion of the emanation. In all three radio-elements a part of the radioactivity is non-separable, and this part consists only of  $\alpha$  rays. The  $\beta$  rays only result at the last stages of the process that can be experimentally traced. In all cases the radiation, from any type of active matter, is a measure of the amount of the next type produced. Thus the radioactivity of ThX at any period throughout its life is always a measure of the amount of emanation it produces.

These results find their explanation if it is supposed that the  $\alpha$  particles projected form integral portions of the atom of the radioactive element. Thus ThX is thorium minus one or more projected  $\alpha$  particles. The emanation similarly is ThX less a further  $\alpha$  particle, and so on. The non-separable activity is due to the atoms of the original radio-element disintegrating at a constant rate. The whole of the processes take place unaltered in velocity, apparently under all conditions of temperature, state of aggregation, and chemical combination. This is to be expected of a subatomic change in which one system only is involved at each change. On this view the spontaneous heat-emission of solid radium-salts, discovered by Curie, is explained by the internal bombardment by the  $\alpha$  particles shot off and absorbed in the mass of the substance.

The amount of energy given out in these subatomic changes is enormous, and from Curie's experiments it can be deduced that each gram of radium gives out  $10^9$  gram-calories during its life, which is sufficient to raise 500 tons a mile high. It seems probable that the internal energy of atoms in general is of a similar high order of magnitude.

## DISCUSSION.

Sir OLIVER LODGE congratulated Prof. Rutherford and Mr. Soddy upon the field of research which had opened up to them and upon the way they were pursuing it. Referring to the fact that the temperature of a piece of radium is above that of its surroundings, he said that Prof. Rutherford's discovery that atoms of matter were thrown out by radium at one-tenth the speed of light would account for energy-effects, and he thought it necessary that when energy passed from an unrecognized atomic to an irregular molecular form, that previously non-existent heat would be produced. The important point in Prof. Rutherford's work was that he had established the fact that one kind of matter is thrown off by another kind of matter, and had also measured the velocity and weight of the particles thus thrown off. We were accustomed to electrons being shot out by matter, but the proof that light atoms were thrown off from heavy atoms was the evolution or transmutation of matter experimentally demonstrated. The heavy atoms of radium appear to collapse and throw off atoms of low atomic weight; the remainder is unstable, and more matter is thrown off, the original atom getting, it is to be presumed, lighter and lighter—according to the view of the author of the paper. It might be thought that this hypothesis about the degradation and the instability of the atoms was mere speculation, but it was the most reasonable explanation of observed phenomena. And the reason he was thus cordially willing to accept it as a working hypothesis was because he had been indistinctly looking for some such effect, being guided thereto by pure theory. And that was the chief point he wished to bring forward.

According to an electric theory of matter, *i. e.* on the view that an atom contained electrons with rapid interatomic movements obeying laws like astronomical laws, this instability ought to exist. Taking a formula by Prof. Larmor for the radiating power of an accelerated electric charge, Sir Oliver Lodge gave a rough proof of the latter statement (reproduced in 'Nature' for June 11th). He stated, in conclusion, as a working hypothesis that we must not suppose that atoms are permanent and eternal, and suggested

that we may possibly find a rise and decay in ordinary matter, and find that the history of an atom may be written—in accordance with the analogy of solar systems and cosmic configurations generally. On the electric theory of matter the falling together of electrons might produce the electric aggregate called an atom, and its subsequent gradual decay or separation into other forms would be accompanied by epochs of radioactivity.

Prof. W. E. AYRTON, after congratulating the author, said he would like to ask a question. Prof. Rutherford had shown us the discharge of an electroscope when a thick plate of metal was placed between a piece of radium and the instrument. Would the electroscope be affected if a piece of radium *completely* surrounded by an earthed *metal* casing was brought near to it? Again, if a piece of radium was insulated inside a completely-closed metal box, would an electroscope, metallically connected with the outside of the box—the whole being placed in a very good vacuum—be charged, and if so, what would be the sign of the charge?

Prof. EVERETT found it difficult to believe that there was a sufficient store of energy in the atom to account for the effects observed. He asked if the phenomena were not due to resonance, the radium atoms being shaken asunder by vibrations in the ether to which they were responsive. These scattered atoms might knock asunder some of the atoms of neighbouring bodies, and so produce the  $\beta$  rays.

Prof. S. P. THOMPSON pointed out that the notion of energy within the atom was based upon the statement that the temperature of a piece of radium was above the temperature of its surroundings. Without doubting the work of Curie, he thought that critical experiments should be made on this point before it could be looked upon as an accepted fact, or such large generalizations be based upon it.

Dr. LOWRY called attention to the slender evidence on which the theory of atomic degradation had been based. The behaviour of thorium and ThX was precisely analogous to that of a substance like  $\pi$  bromo-nitrocamphor, which exists in an inactive "normal" form as a neutral substance and a dielectric, but also in an active "pseudo" form in which it is a strong acid and an electrolyte. Both forms are fairly

stable in the solid state, but when dissolved are exceedingly labile, and the merest trace of impurity is sufficient to bring about an isomeric change which leads in the course of a few days or hours to a condition of equilibrium in which there are about 94 parts of the inactive normal to 6 parts of the active pseudo form. The curves representing the rate of recovery and decay of (electrolytic) activity are mathematically identical with those shown for the recovery and decay of radioactivity by the two modifications of thorium and uranium. There is, therefore, the strongest evidence in favour of the view that the conversion of thorium into ThX is a *reversible change*, and that the emanations and excited activity are merely physical phenomena.

Prof. RUTHERFORD, in reply to Prof. Ayrton, said that in the first case discharge would take place, and that the result in the second case would depend upon the thickness of the walls, and therefore upon the nature of the rays which could pass through. He also pointed out that Dr. Lowry's explanation involved him in perpetual motion. It did not explain radioactivity, and it was difficult to see how it could account for the phenomena occurring in stages. Moreover, there was no reversible chemical action that went on at the same rate at a red heat as in liquid air. With regard to Prof. Everett's suggestion, it seemed that such a process would be even more wonderful than that suggested. The phenomena go on unchanged even when the substance is shielded from external influence by many inches of lead. He felt confident that Curie's observation of heat emission would prove to be well founded.

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FIG. 5.

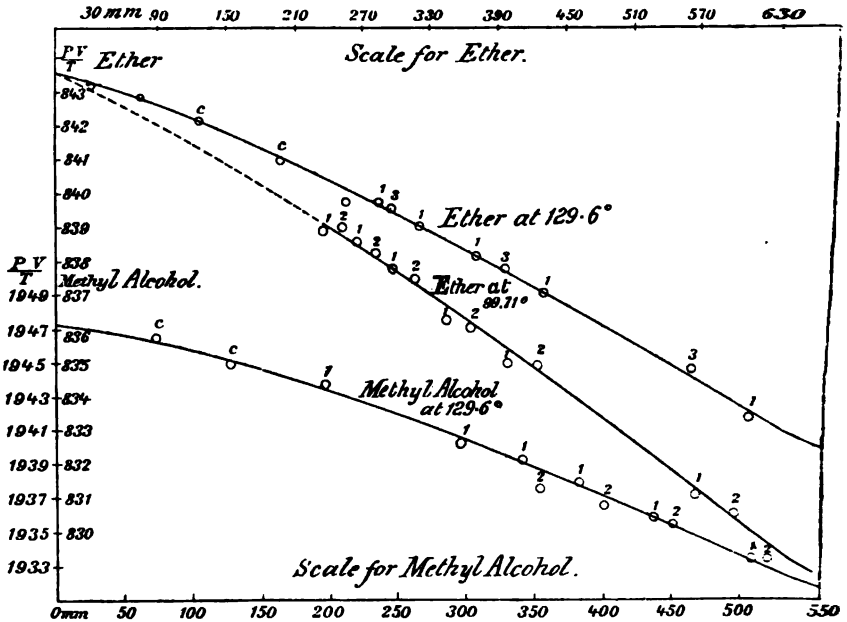
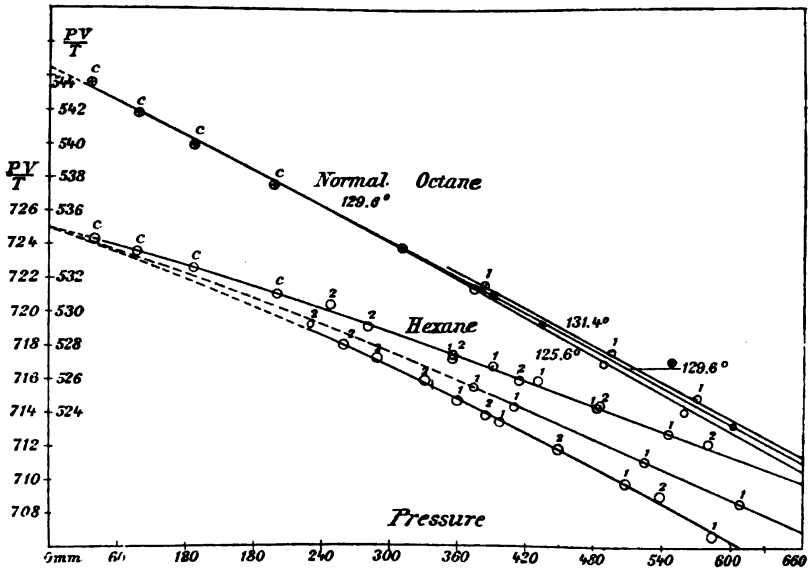


FIG. 7.





**FIG. 6.**

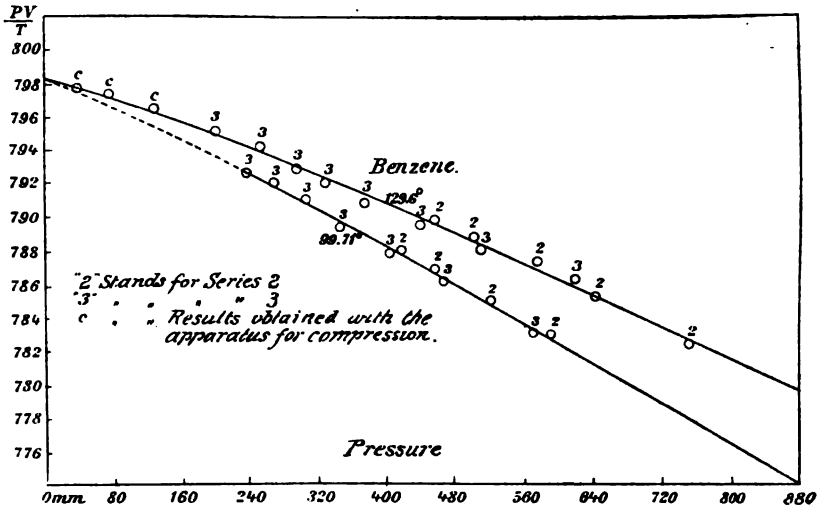


FIG. 8.

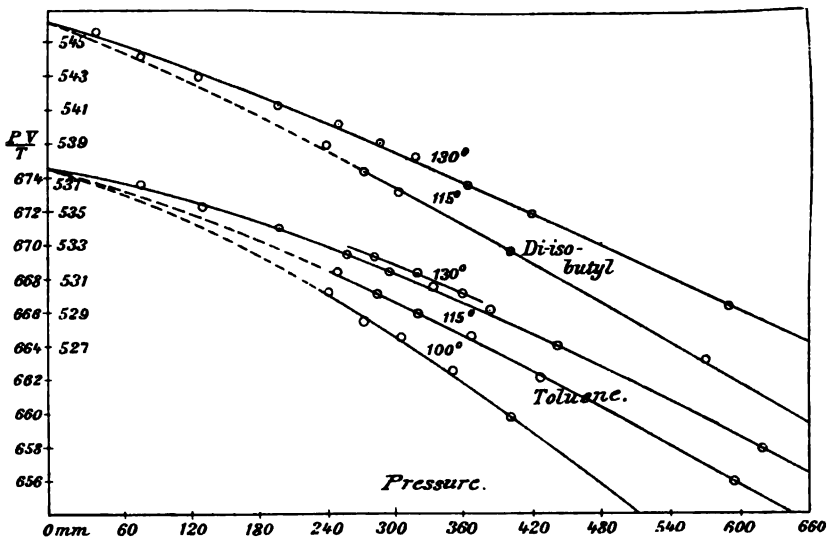






FIG. 1.

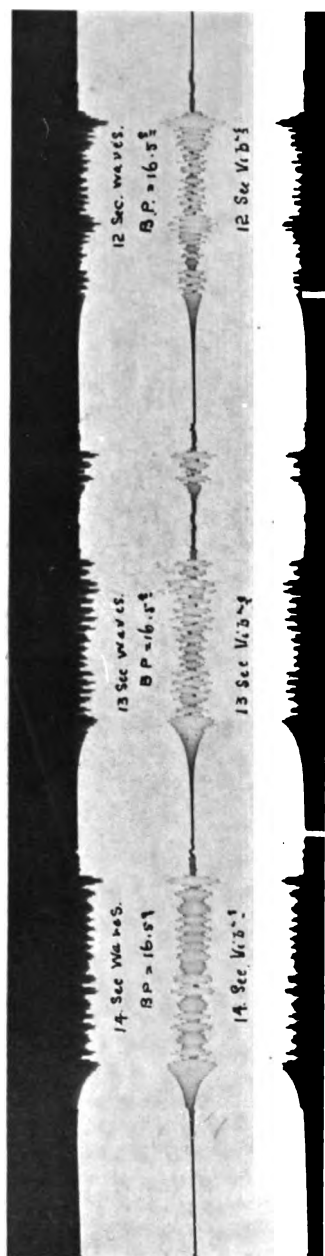


FIG. 2.

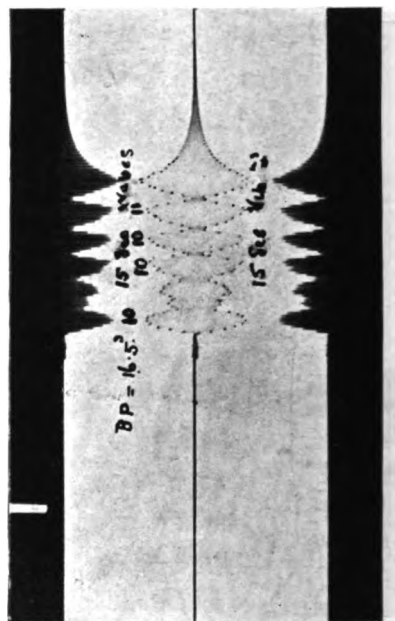


FIG. 3.

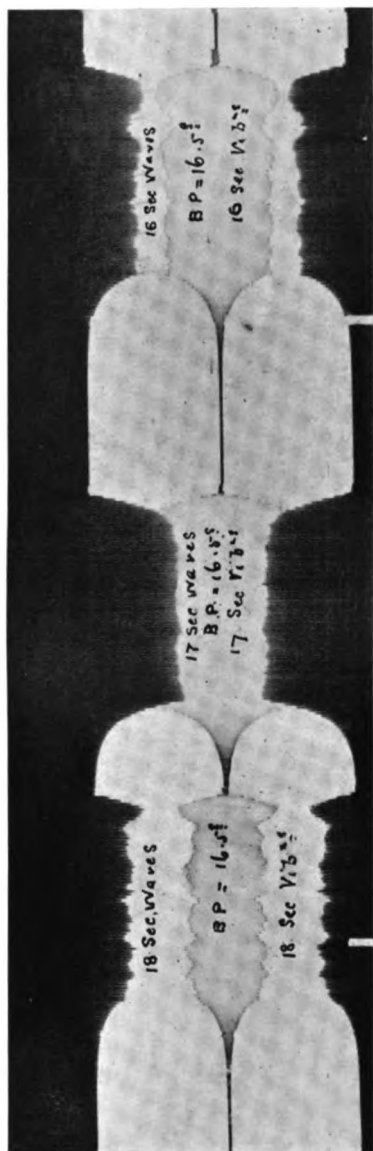
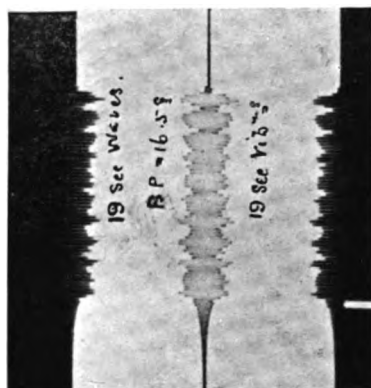


FIG. 4.



CE L  
KESL

*in m*

*d*

*in m*

3

*in m*

0

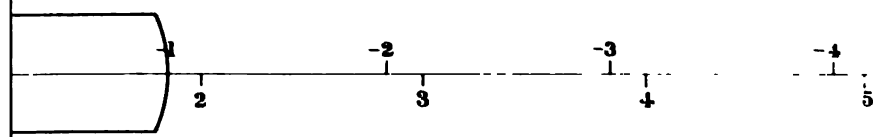
1

*in m*

# CE LENSES.

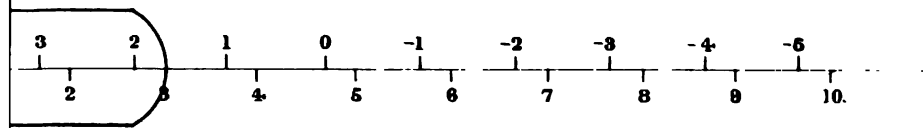
KESLEY.

Direction of Light  
in<sup>m</sup> dev<sup>n</sup> for rays from  $\alpha^u$



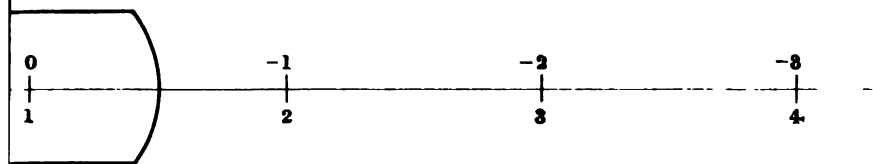
$$f = -\frac{7}{12} d$$

in<sup>m</sup> dev<sup>n</sup> for rays from  $\alpha^4$



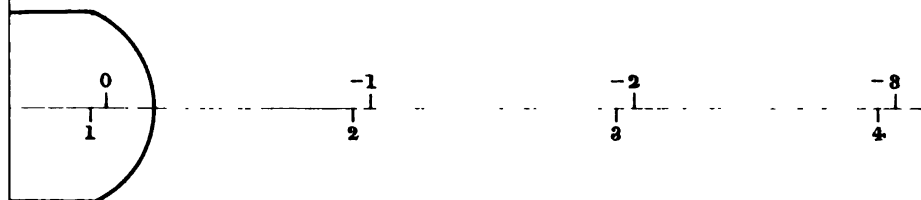
$$f = -\frac{d}{4}$$

in<sup>m</sup> f or  $\frac{df}{du} = 0$



$$f = -\frac{2}{3} d$$

uiconvex



$$f = -\frac{25}{36} d$$





**PROCEEDINGS**  
**AT THE**  
**MEETINGS OF THE PHYSICAL SOCIETY**  
**OF LONDON.**  
**SESSION 1901-1902.**

---

**February 22nd, 1901.**

**Meeting held at Burlington House.**

**The PRESIDENT in the Chair.**

**The following were elected Fellows of the Society :—**

**J. HENRY, W. MAKOWER, A. E. TUTTON.**

**The following Papers were read :—**

- 1. How Air subjected to X-rays loses its Discharging Property, and how it discharges Electricity. By Prof. E. VILLARI, Hon. Fellow of the Society.**
  - 2. On the Propagation of Cusped Waves and their Relation to the Primary and Secondary Focal Lines. By Prof. R. W. WOOD.**
  - 3. On Cyanine Prisms, and a new method of exhibiting Anomalous Dispersion. By Prof. R. W. WOOD.**
- 

"

March 8th, 1901.

Meeting held at Burlington House.

Dr. GLAZE BROOK in the Chair.

The following was elected a Fellow of the Society :—

Prof. J. CHUNDER BOSE.

The following Paper was read :—

1. A Theory of Colloidal Solution. By Dr. F. G. DONNAN.

Mr. R. APPELYARD exhibited :—

1. A Slide Bridge for testing the Conductivity of Metals.

2. A Mechanical Gauge for checking the Diameters of Spheres.

3. An Electric Lamp for Reflecting Instruments.

March 22nd, 1901.

Meeting held at University College.

The PRESIDENT in the Chair.

The following were elected Fellows of the Society :—

H. BEGE and E. SMART.

The following Papers were read :—

1. On the Expansion of Silica. By Prof. H. L. CALLENDAR, F.R.S.

2. Description of the Spectroscopic Apparatus at University College. By E. C. C. BALY.

Exhibition of Apparatus took place in the Chemical Laboratory of University College.

April 26th, 1901.

Meeting held at Burlington House.

Dr. GLAZE BROOK in the Chair.

The following Papers were read :—

1. On the Thermodynamical Correction of the Gas Thermometer. By Prof. H. L. CALLENDAR, F.R.S.

2. On the production of a Bright-line Spectrum by Anomalous Dispersion, and its Application the "Flash-Spectrum." By Prof. R. W. WOOD.

May 10th, 1901.

Meeting held at Burlington House.

The PRESIDENT in the Chair.

The following were elected Fellows of the Society:—

C. CUTHBERTSON, W. J. GREENSTREET, W. R. KELSEY.

The following Papers were read:—

1. On the Applications of Elastic Solids to Metrology. By Dr. C. CHREE, F.R.S.
  2. On the Thermal Properties of Isopentane compared with those of Normal Pentane. By J. ROSE-INNES and Dr. S. YOUNG.
- 

May 31st, 1901.

Meeting held at Burlington House.

The PRESIDENT in the Chair.

The following Papers were read:—

1. On the Resistance of Dielectrics, and the Effect of an Alternating Electromotive Force on the Insulating Properties of India-rubber. By A. W. ASHTON.
  2. On a Model which imitates the behaviour of a Dielectric. By Prof. J. A. FLEMING and A. W. ASHTON.
  3. On the Electrification of Indiarubber by Extension and Percussion. By A. W. ASHTON.
- 

June 14th, 1901.

Meeting held at Burlington House.

The PRESIDENT in the Chair.

The following were elected Fellows of the Society:—

J. M. McEWEN and F. J. SELBY.

The following Papers were read:—

1. On Herr Jahn's Measurements of the Electromotive Force of Concentration Cells. By Dr. R. A. LEHFELDT.
  2. On the Mechanism of Radiation. By J. H. JEANS.
-

June 28th, 1901.

Meeting held at King's College.

Prof. J. D. EVERETT in the Chair.

The following Papers were read:—

1. On the Effect of a High-frequency Oscillating Field on Electrical Resistance. By S. A. F. WHITE.

2. On the Spectrum of Cyanogen. By E. C. C. BALY and Dr. H. W. SYERS.

An Exhibition of the Laboratory and Museum at King's College by S. A. F. WHITE.

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October 26th, 1901.

Meeting held at Burlington House.

The PRESIDENT in the Chair.

The following was elected a Fellow of the Society:—

J. H. JEANS.

The following Papers were read:—

1. On the Variation with Temperature of the Thermoelectromotive Force, and of the Electric Resistance of Nickel, Iron, and Copper, between the Temperatures of  $-200^{\circ}$  and  $+1050^{\circ}$ . By E. P. HARRISON.

2. On Asymmetry of the Zeeman Effect. By G. W. WALKER.

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November 8th, 1901.

Meeting held at Burlington House.

Mr. T. H. BLAKESLEY in the Chair.

The following Papers were read:—

1. On a Voltameter for Small Currents. By Dr. R. A. LEHFELDT.

2. Note on a paper by Prof. Fleming and Mr. Ashton on a Model which imitates the behaviour of Dielectrics. By Dr. J. BUCHANAN.

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November 22nd, 1901.

Meeting held at Burlington House.

The PRESIDENT in the Chair.

A Special General Meeting was held at which the following Resolution was passed :—

*Resolution* :—"That the Five Hundred Pounds Ordinary Stock (fully paid up) in the London, Brighton, and South Coast Railway Company, offered to the Society by WILLIAM FORD STANLEY, Esq. (a Fellow), be accepted and retained, the said Stock being hereby approved of as an investment in pursuance of No. 93 of the Articles of Association. And that the said W. F. Stanley be requested to transfer the same Stock into the name of the Society to be held upon the trusts declared by a Deed Poll which has been already prepared and approved, and that the Seal of the Society be affixed to such Deed Poll."

The following was elected a Fellow of the Society :—

B. HOPKINSON.

The following Papers were read :—

1. A Multiple Transmission Fixed Arm Spectroscope. By Prof. W. CASSIE.
2. Measurement of Young's Modulus. By Prof. W. CASSIE.
3. Notes on Gas Thermometry. By Dr. P. CHAPPUIS.

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December 13th, 1901.

Meeting held at Burlington House.

The PRESIDENT in the Chair.

The following Papers were read :—

1. On Circular Filaments or Circular Magnetic Shells equivalent to Circular Coils, and on the equivalent Radius of a Coil. By Prof. T. R. LYLE.
  2. On Air Pressures used in playing Brass Instruments. By Dr. E. H. BARTON and S. C. LAWS.
  3. Note on a new Hygrometric Method. By E. B. H. WADE.
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January 22nd, 1902.

Meeting held at Burlington House.

The PRESIDENT in the Chair.

The following were elected Fellows of the Society :—

M. E. J. GHEURY, M. O'GORMAN, F. P. SEXTON.

The following Paper was read :—

On the Factors of Heat. By J. SWINBURNE.

Mr. EUSTACE H. LARGE exhibited some Twinned Crystals of Selenite.

*Annual General Meeting.*

February 14th, 1902.

Mr. T. H. BLAKESLEY in the Chair.

The following Report of the Council was read by the Secretary :—

The year 1901 has not been an eventful one to the Society. The Meetings have been held with regularity, and the attendance quite equals that of the preceding years. Those falling on March 22nd and June 25th were held respectively in University College and King's College, by the kind permission of Profs. Callendar and Ramsay and Prof. Adams.

The number of Fellows on the roll remains unchanged since last year. The Society has had to mourn the loss of Principal J. Viriamu Jones and Dr. Shettle by death; and there have been five resignations and four names removed for non-payment of subscriptions. Eleven new Fellows have been elected. The Society has also lost by death two of the Honorary Fellows, Prof. Rowland of Baltimore, and Dr. Rudolph Koenig of Paris, who was only elected at the last Anniversary Meeting,

On the occasion of the ninth Jubilee of the University of Glasgow in June 1901, the Physical Society was invited to send a Delegate, and was represented by the President. An illuminated address of congratulation was presented on that occasion.

More recently, on January 12th, 1902, our Honorary Fellow, Prof. Hittorf, of Münster, attained the Jubilee of his Professorship of Physics in the University of that city; a telegram of congratulation was sent to him in the name of the Physical Society.

The chief event of the year was the generous gift by Mr. W. F. Stanley to enable the Society to send out a short *résumé* of the

Proceedings at each meeting to every Fellow. Mr. Stanley's wishes have been carried out since the opening of the Session. Your Council feel that the issue of this bulletin will tend to bind the Fellows of the Society together, and to increase their appreciation of the value to the Society of Mr. Stanley's generous action.

The Report of the Council was received.

The Treasurer read his Report and presented the Balance Sheet, which were received.

The election of Officers and other Members of Council then took place, the new Council being constituted as follows :—

*President.*—Prof. S. P. THOMPSON, D.Sc., F.R.S.

*Vice-Presidents who have filled the Office of President.*—Dr. J. H. GLADSTONE, F.R.S.; Prof. G. C. FOSTER, F.R.S.; Prof. W. G. ADAMS, M.A., F.R.S.; Lord KELVIN, D.C.L., LL.D., F.R.S.; Prof. R. B. CLIFTON, M.A., F.R.S.; Prof. A. W. REINOLD, M.A., F.R.S.; Prof. W. E. AYRTON, F.R.S.; Prof. A. W. RÜCKER, M.A., D.Sc., F.R.S.; Sir W. DE W. ABNEY, R.E., K.C.B., D.C.L., F.R.S.; SHELFOED BIDWELL, M.A., LL.B., F.R.S.; Principal OLIVER J. LODGE, D.Sc., F.R.S.

*Vice-Presidents.*—T. H. BLAKESLEY, M.A.; Prof. J. D. EVERETT, D.C.L., F.R.S.; S. LUPTON, M.A.; J. WALKER, M.A.

*Secretaries.*—H. M. ELDER, M.A.; W. WATSON, B.Sc., F.R.S.

*Foreign Secretary.*—R. T. GLAZEBROOK, D.Sc., F.R.S.

*Treasurer.*—Prof. H. L. CALLENDAR, M.A., F.R.S.

*Librarian.*—W. WATSON, B.Sc., F.R.S.

*Other Members of Council.*—C. CHREE, D.Sc., F.R.S.; W. R. COOPER, M.A.; G. GRIFFITH, M.A.; R. A. LEHFELDT, D.Sc.; A. W. PORTER, B.Sc.; W. A. PRICE, M.A.; W. N. SHAW, M.A., F.R.S.; W. F. STANLEY, F.G.S.; J. SWINBURNE; A. A. CAMPBELL SWINTON, M.I.C.E.

The following were elected Honorary Fellows of the Society :—

Prof. S. P. LANGLEY and Prof. H. A. LORENTZ.

The PRESIDENT of the German Physical Society was elected an *ex-officio* Fellow of the Society.

Votes of thanks were passed to the Auditors, the Officers and Council, and to the Chemical Society.

An Ordinary Science Meeting then took place, at which Mr. T. H. LITTLEWOOD exhibited an improved form of Atwood's Machine.

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#### TREASURER'S REPORT.

The number of Members has remained practically constant at 410, but the amount received in subscriptions and donations has increased from £407 in 1900 to nearly £700. Part of this increase is accounted for by the generous response of many of the life-members to an Appeal issued in the early part of the year; £104 was received in compositions and donations from this source, and 24 new annual subscribers of one guinea were secured; £100 was transferred to the Guarantee Fund on deposit, which now amounts with interest to about £569, representing contributions made to assist the Society in the publication of 'Science Abstracts.' There were also two life-compositions of 30 guineas each from new Members. The amount realized in collecting arrears of subscriptions, namely £79, considerably exceeded the estimate of £42 made last year. The amount collected for current subscriptions in 1901 was £56 in excess of that collected in 1900, and the arrears now due are much less than usual. The greater part of the increase of receipts is of a temporary character, but there is a nett increase of revenue of about £50, which will probably be maintained. The amount paid for printing, £287 12s., is unusually large, but includes a liability of £71 outstanding from last year, so that the actual expenditure for 1901 was less than that for 1900. The bill for periodicals covers a period of 4 years, extending to the end of 1902. Omitting exceptional sources of revenue and expenditure, there remains a margin on the right side, which may be utilized in future years for extending the sphere of activity of the Society.





# PROPERTY ACCOUNT OF THE PHYSICAL SOCIETY, DECEMBER 31, 1901.

ASSETS.		LIABILITIES.	
	£ s. d.		£ s. d.
Subscriptions due, estimated .....	25 0 0	Chemical Society, Rent for 1901 .....	12 12 0
£533 Furness 3 per cent. Debenture Stock .....	493 0 0	Periodicals (1902) .....	0 10 0
£1600 Midland Railway 2½ per cent. Preference Stock .....	1280 0 0	Balance .....	3986 3 5
£200 Metropolitan Board of Works 3½ per cent. Consolidated Stock .....	218 0 0		
£400 Lancaster Corporation 3 per cent. Stock .....	376 0 0		
£259 2s. 9d. New South Wales 3½ per cent. Inscribed Stock .....	289 0 0		
Balance in the Bank .....	167 13 3		
"    on Deposit .....	561 6 4		
Interest due on Deposit .....	7 10 10		
Publications in Stock, estimated .....	600 0 0		
Due for Dinner .....	1 15 0		
	<u>£3999 5 5</u>		<u>£3999 5 5</u>

Securities examined and verified.

W. R. PIDGEON, }  
L. R. SHOETER, } *Auditors.*

Audited and found correct,

HUGH L. CALLENDAR, *Treasurer.*

W. R. PIDGEON, }  
L. R. SHOETER, } *Auditors.*

PROCEEDINGS  
AT THE  
MEETINGS OF THE PHYSICAL SOCIETY  
OF LONDON.  
SESSION 1902-1903.

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February 28th, 1902.

Meeting held at Burlington House.

The PRESIDENT in the Chair.

The following were elected Fellows of the Society :—

J. M. MCG. BARR, G. M. GRACE, H. R. NOBLE, J. SCHOFIELD.

The following Papers were read :—

1. On Focal Lines and Anchor-ring Wave-fronts. By Prof. J. D. EVERETT.
2. Contributions to the Theory of the Resolving Power of Objectives. By Prof. J. D. EVERETT.
3. On the Absorption, Dispersion, and Surface Colour of Selenium. By Prof. R. W. WOOD.

The PRESIDENT exhibited some Mirrors of Tellurium.

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March 14th, 1902.

Meeting held at Burlington House.

Mr. S. LUTTON, Vice-President, in the Chair.

The following Papers were read :—

1. On the Thermal Expansion of Porcelain. By A. E. TUTTON.
  2. On the Temperature Variation of the Electrical Resistances of Pure Metals, and Allied Matters. By W. WILLIAMS.
  3. On a Suspected Case of the Electrical Resonance of Minute Metal Particles for Light Waves. A new Type of Absorption. By Prof. R. W. WOOD.
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April 11th, 1902.

Meeting held at Burlington House.

The PRESIDENT in the Chair.

The following was elected a Fellow of the Society :—

J. R. ERSKINE MURRAY.

The following Papers were read :—

1. On the Use of Kathode Rays for Alternate Current Measurements. By Dr. J. T. MORRIS.
2. On an Experiment on the Current Growth in an Inductive Circuit. By Dr. J. T. MORRIS.

Dr. LEHFELDT exhibited an Electric Heater.

Mr. GRANT exhibited an Apparatus for Vapour-Pressure Measurements.

Mr. W. B. CROFT exhibited :—

- (a) Some methods of graphically solving the Equations of a Lens.
  - (b) A method of solving a Quadratic.
  - (c) Prof. Weinhold's Apparatus for distributing a Continuous Current into a Three-phase System.
  - (d) Examples of the Regular Solids in Crystals.
  - (e) Testing a Plane Surface.
  - (f) An Electric Lamp with a flat filament.
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April 25th, 1902.

Meeting held at Burlington House.

The PRESIDENT in the Chair.

The following Paper was read:—

A Note on the Compound Pendulum. By S. A. F. WHITE.

Dr. DAWSON TURNER exhibited a Mechanical Break for Induction Coils, and showed some Experiments on the Transparency of Materials to Ultra-Violet Light.

Mr. WILSON NOBLE exhibited a Mechanical Break for Induction Coils.

Mr. R. S. WHIPPLE exhibited a Temperature Indicator for use with Platinum Thermometers, in which Readings are Automatically reduced to the Gas Scale.

May 9th, 1902.

Meeting held at Burlington House.

Prof. REINOLD, Vice-President, in the Chair.

The following was elected a Fellow of the Society:—

A. WHITWELL.

The following Paper was read:—

On an Electrical Micrometer. By Dr. P. E. SHAW.

May 23rd, 1902.

Meeting held at Burlington House.

The PRESIDENT in the Chair.

The following Papers were read:—

1. The Ebullition of Rotating Water. By T. C. PORTER.

Mr. BOYS showed an experiment bearing on the Paper.

2. On the Conservation of Entropy. By J. A. ERSKINE.

3. On Rational Units of Electromagnetism. By Signor GIORGI.

June 13th, 1902.

Meeting held at the National Physical Laboratory.

The PRESIDENT in the Chair.

Dr. GLAREBROOK described the arrangement and objects of the Laboratory.

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June 20th, 1902.

Meeting held at Burlington House.

The PRESIDENT in the Chair.

The following Papers were read:—

1. On the Heat absorbed when a Liquid is brought into Contact with a Finely-divided Solid. By C. J. PARKS.

2. On the Electrical Resonance of Metal Particles for Light Waves. By Prof. R. W. WOOD.

3. On a Remarkable case of Uneven Distribution of Light in a Diffraction-Grating Spectrum. By Prof. R. W. WOOD.

Mr. G. F. HERBERT SMITH exhibited a Three-Circle Goniometer.

Prof. CALLENDAR exhibited a Simple Form of Apparatus for Measuring the Mechanical Equivalent of Heat.

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October 31st, 1902.

Meeting held at Burlington House.

The PRESIDENT in the Chair.

The following Papers were read:—

1. On the Existence of a Relationship between the Spectra of some Elements and the Squares of their Atomic Weights. By Dr. W. MARSHALL WATTS.

2. On the Size of Atoms. By H. V. RIDOUT.

Prof. CALLENDAR exhibited some Vacuum Calorimeters.

Miss EVERETT exhibited some Photographs of Cross Sections of Hollow Pencils formed by Oblique Transmission through an Annulus of a Lens.

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November 14th, 1902.

Meeting held at Burlington House.

The PRESIDENT in the Chair.

The following Papers were read :—

1. On the Theory of the Aluminium Electrode. By J. K. H. INGELIS and Dr. W. W. TAYLOR.

2. On a Determination of the Ratio of the Specific Heats at Constant Pressure and at Constant Volume for Air and Steam. By W. MAKOWER.

Prof. CALLENDAR exhibited a Regulator for a Current of Steam.

November 28th, 1902.

Meeting held at Royal College of Science.

The PRESIDENT in the Chair.

The following were elected Fellows of the Society :—

W. H. ECCLES, M. FINN, S. J. WHITAKER.

The following Paper was read :—

On a Slide-Rule for Powers of Numbers. By Prof. PERRY.

Prof. CALLENDAR exhibited a Lecture Experiment to determine the Value of the Mechanical Equivalent of Heat.

December 12th, 1902.

Meeting held at Burlington House.

Mr. LUPTON, Vice-President, in the Chair.

The following Papers were read :—

1. On a Portable Capillary Electrometer. By S. W. J. SMITH.

2. On Astigmatic Aberration. By R. J. SOWTER.

3. On Vapour-Density Determinations. By Prof. Sir W. RAMSAY and Dr. STEELE.

Prof. WILBERFORCE exhibited a Lecture Experiment on Diffusion.

January 23rd, 1903.

Meeting held at Burlington House.

The PRESIDENT in the Chair.

The following was elected a Fellow of the Society:—

Prof. T. R. LYLE.

The following Papers were read:—

1. Note on an Elementary Treatment of Conducting Networks.  
By Prof. WILBERFORCE.

2. On the Theory of the Quadrant Electrometer. By G. W. WALKER.

Mr. W. H. DERRIMAN exhibited an Oscillating Table for determining Moments of Inertia.

*Annual General Meeting.*

February 13th, 1903.

Meeting held at Burlington House.

The PRESIDENT in the Chair.

The following Report of the Council was read by the Secretary:—

Since the last Annual General Meeting of the Society the usual number of Meetings has been held. One of these, on June 13th, 1902, was held at the National Physical Laboratory at Bushy House, on the kind invitation of the Director, and was well attended in spite of a downpour of rain; another, on November 28th, was held at the Royal College of Science, by the invitation of Prof. Callendar; and that which should have been held on June 27th took place on June 20th, owing to the fact that the former day had been declared a National Holiday.

The Society has to mourn the loss of several Fellows by death. Among these occur the names of Sir F. Abel, Dr. J. H. Gladstone, the first President of the Society, Mr. G. Griffith, long an active member of the Council, Sir W. Chandler Roberts-Austen, first Secretary of the Society, and Mr. James Wimshurst. Memoirs of some of these will be found in the Proceedings. Prof. Cornu and Prof. R. Felici, Hon. Fellows of the Society, also died during the year.

The Council also regrets that, owing to the calls of business,



Mr. Elder has found it necessary to resign the post of Secretary. They feel that the Society owes a debt of gratitude to Mr. Elder for the energy and devotion with which he has ministered to the interest of the Society during the last decade.

There have been four resignations, and eleven new Fellows have been elected. The numbers are therefore well maintained.

The Bulletins of the Proceedings of the Meetings have been sent out regularly in accordance with the terms of Mr. Stanley's generous gift to the Society.

A new agreement for a term of three years has been arranged between the Society and the Institution of Electrical Engineers to provide for the continuation of 'Science Abstracts,' and it is hoped that the usefulness of this publication will be thereby increased.

The Report of the Council was received.

The Treasurer read his Report and presented the Balance Sheet, which were received.

The election of Officers and other Members of Council then took place, the new Council being constituted as follows :—

*President.*—R. T. GLAZEBROOK, D.Sc., F.R.S.

*Vice-Presidents who have filled the Office of President.*—Prof. G. C. FOSTER, F.R.S.; Prof. W. G. ADAMS, M.A., F.R.S.; The Lord KELVIN, D.C.L., LL.D., F.R.S.; Prof. R. B. CLIFTON, M.A., F.R.S.; Prof. A. W. REINOLD, M.A., F.R.S.; Prof. W. E. AYRTON, F.R.S.; Prin. Sir ARTHUR W. RUCKER, M.A., D.Sc., F.R.S.; Sir W. DE W. ABNEY, R.E., K.C.B., D.C.L., F.R.S.; SHELFORD BIDWELL, M.A., LL.B., F.R.S.; Prin. Sir OLIVER J. LODGE, D.Sc., F.R.S.; Prof. S. P. THOMPSON, D.Sc., F.R.S.

*Vice-Presidents.*—T. H. BLAKESLEY, M.A.; Prof. J. D. EVERETT, D.C.L., F.R.S.; S. LUPTON, M.A.; J. SWINBURNE.

*Secretaries.*—W. WATSON, D.Sc., F.R.S.; W. R. COOPER, M.A.

*Foreign Secretary.*—Prof. S. P. THOMPSON, D.Sc., F.R.S.

*Treasurer.*—Prof. H. L. CALLENDAR, M.A., F.R.S.

*Librarian.*—W. WATSON, D.Sc., F.R.S.

*Other Members of Council.*—C. CHREE, D.Sc., F.R.S.; W. B. GROFF, M.A.; F. G. DONNAN, M.A., Ph.D.; H. M. ELDER, M.A.;

R. A. LEHFELDT, D.Sc. ; Prof. J. PERRY, D.Sc., F.R.S. ; A. W. PORTER, B.Sc. ; W. A. PRICE, M.A. ; W. F. STANLEY, F.G.S. W. C. D. WHETHAM, M.A., F.R.S.

Votes of thanks were passed to the Auditors, the Officers and Council, and to the Chemical Society.

The following were elected Honorary Fellows of the Society :—

M. HENRI BECQUEREL and Prof. AUG. RIGHI.

The following were elected Fellows of the Society :—

J. RHEINBERG, W. E. TEMPLETON, W. S. TUCKER,

C. J. L. WAGSTAFF.

The PRESIDENT then delivered his Address.

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#### TREASURER'S REPORT.

The receipts for the present year do not include any exceptional sources of revenue such as life-compositions or donations. On the other hand, there are additional sources of expenditure : (1) on the International Catalogue, £16 4s. 9d. ; (2) on the printing and distribution of abstracts of proceedings, about £35. In spite of this the bill for printing has been somewhat below the average, so that the revenue has just balanced the expenditure. The difference between the bank balance of £167 13s. 3d. at the beginning of the year, and the balance of £68 6s. 6d. at the end of the year, is satisfactorily accounted for by the investment of about £98 from the current account, in addition to £571 10s. 5d. from the deposit account, in the purchase of Great Eastern Railway Debentures. By this purchase and the gift of L. B. & S. C. Railway Stock from Mr. W. F. Stanley, the revenue of the Society from investments has been materially increased, and will next year amount to about £115. The payments made to 'Science Abstracts' next year will be reduced to about £256, under the new agreement with the Institution of Electrical Engineers. Thus, although some increase in the printing bill may be expected, it is probable that the revenue will continue to balance the expenditure.

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THE TREASURER IN ACCOUNT WITH THE PHYSICAL SOCIETY, FROM JANUARY 1ST, 1902, TO DECEMBER 31ST, 1902.

[illegible]

**HUGH L. CALLENDAR, Honorary Treasurer.**

**Audited and found correct.**

9th January, 1903.

LEWIS R. SHORTER,  
R. MULLINEUX WALMSLEY,

} *Auditors.*

# PROPERTY ACCOUNT OF THE PHYSICAL SOCIETY, DECEMBER 31, 1902.

ASSETS.		LIABILITIES.	
	£ s. d.		£ s. d.
Subscriptions due, estimated .....	87 16 0	Royal Asiatic Society.....	2 2 0
£533 Furness 3 per cent. Debenture Stock .....	490 0 0	Cheque not presented.....	1 11 5
£1600 Midland Railway 2½ per cent. Preference Stock .....	1232 0 0	Balance .....	4615 9 1
£200 Metropolitan Board of Works 3½ per cent. Consolidated Stock .....	212 0 0		
£400 Lancaster Corporation 3 per cent. Stock .....	380 0 0		
£259 2s. 9d. New South Wales 3½ per cent. Inscribed Stock .....	259 0 0		
£800 London, Brighton, and South Coast Railway Ordinary Stock .....	705 0 0		
£500 Great Eastern Railway 4 per cent. Debenture Stock .....	635 0 0		
Publications in Stock, estimated .....	600 0 0		
Balance in Bank.....	68 6 6		
	<u>£4619 2 6</u>		<u>£4619 2 6</u>

HUGH L. CALLENDAR, *Honorary Treasurer.*

Audited and found correct,

LEWIS R. SHOETER, }  
 944 Jan., 1903. R. MULLINEUX WALMSLEY, } *Auditors.*

Securities examined and verified.

LEWIS R. SHOETER, }  
 944 Jan., 1903. R. MULLINEUX WALMSLEY, } *Auditors.*

## OBITUARIES.

Sir FREDERIC AUGUSTUS ABEL, Bart., G.C.V.O., K.C.B., F.R.S.

Sir Frederic Abel was the eldest son of the late J. L. Abel, of Kennington, a music master of German descent, and was born in London on the 17th July, 1827. He began his studies in 1844 under Dr. Ryan at the Royal Polytechnic Institution; but in the following year he entered as one of the twenty-six original students of the Royal College of Chemistry under Hofmann. Here he soon became one of the assistants, and in 1851 Demonstrator of Chemistry at St. Bartholomew's Hospital. Two years later he succeeded Faraday as lecturer on Chemistry at the Royal Military Academy, Woolwich, where he became Scientific Adviser to the War Office, and was soon appointed Chemist of the War Department, with official residence at Woolwich. At this time he wrote with Bloxam a 'Handbook of Chemistry,' which has passed through many editions and is now known as Bloxam's 'Chemistry.' During his long connection with Woolwich (up till 1887) he was in close touch with all the vast changes which have taken place in modern warfare and explosives. From 1887 to 1901 he was Organizing Secretary of the Imperial Institute.

Sir Frederic Abel was a British Representative at the Paris and Vienna Electrical Exhibitions of 1881 and 1883; and was chief of the Executive of the International Inventions and Music Exhibitions held in London in 1885. He was elected President of the Chemical Society 1875-7, President of Section B of the British Association and of the Institution of Electrical Engineers in 1877, President of the Institute of Chemistry in 1881-2, President of the Society of Chemical Industry in 1883, and Chairman of the Society of Arts. In 1883 he was elected an Honorary Member of the Institution of Mechanical Engineers, in recognition of his having undertaken a series of experiments for their Committee on the Hardening of Steel. He was also President of the British Association in 1890, and of the Iron and Steel Institute in 1891. He received the honour of C.B. in 1877, K.C.B. in 1891, and was created a Baronet in 1893, and a Knight Grand Cross of the Victorian Order in 1901.

The original papers by Sir Frederic Abel were chiefly on explosives and kindred subjects.

## JOHN HALL GLADSTONE, D.Sc., F.R.S.

Dr. Gladstone was born in 1827, and studied first under Prof. Graham at University College, London, and then under Baron Liebig at Giessen. From 1850 to 1853 he lectured on Chemistry at St. Thomas's Hospital, and carried out investigations on explosives and phosphorus compounds, resulting in his election to the Royal Society at the early age of 26. In 1869 his paper on "Refraction Equivalents of the Elements" appeared in the 'Philosophical Transactions.' This paper formed a sequel to his research with Dale on the Refraction, Dispersion, and Sensitiveness of Liquids. From 1874 to 1877 Dr. Gladstone was Fullerian Professor of Chemistry at the Royal Institution. In conjunction with Mr. Tribe, Dr. Gladstone discovered the Copper-zinc Couple formed by the deposition of copper on zinc crystals, which is largely used in certain chemical operations. In 1877 he gave a discourse on the "Influence of Chemical Constitution on the Refraction of Light." About this time his researches were chiefly on the action of the copper-zinc couple. In 1880 he published, with Mr. Tribe, a paper on the "Aluminium Iodine Reaction," which was followed by papers on "Thermal Electrolysis" and the "Chemistry of the Secondary Batteries of Planté and Faure." Dr. Gladstone also worked with Dr. W. H. Perkin on Dispersion Equivalents, and with Mr. Hibbert on Electrolysis and Secondary Batteries. The latter papers have added much to our knowledge of the theory of this difficult subject. Their most recent work was on the Molecular Refraction of Dissolved Salts and Acids, bringing out the relationship between change of specific refraction and of electrical conductivity on dilution. They also published papers on the action of metals and their salts on Röntgen rays.

Dr. Gladstone was President of the Physical Society from its formation in 1874 to 1876, President of the Chemical Society from 1877 to 1879, and President of the Education Society from 1880 to 1881. A few years ago he was awarded a Davy medal by the Royal Society.

In addition to scientific work, Dr. Gladstone took an active interest in politics.

## GEORGE GRIFFITH.

George Griffith was born at Llangunner, Carmarthen, in 1833. His father was Canon of St. David's. He was educated at St. David's School and at Jesus College, Oxford, where he took a

First Class in Natural Science in 1856. From 1864 to 1866 he was Science Master at Winchester College, and then Science Master at Harrow from 1867 till 1893. His long official connexion with the British Association for the Advancement of Science began in 1862, when he became Assistant General Secretary. He held this office till 1878, and resumed it in 1890, and this time retained it till his death in May 1902.

He was an original member of the Physical Society of London, and from 1895 till his death he was one of the most assiduous members of the Council. He was elected a Vice-President in 1898. His duties at the British Association brought him into personal contact with nearly all the leading men of science belonging to this country, and with very many of those of other countries; and it is universally recognized that the success which has attended the meetings of the Association for the last forty years was very largely due to his tact and urbanity and to his remarkable knowledge of men and things. He was aided by an unusually exact and ready memory, which made him an unfailing authority on the usages and precedents of the Association.

Though the study of science formed the chief occupation of his life, he kept up his classics and had a wide knowledge of general literature. After giving up school-work at Harrow, he worked hard for several years upon the Royal Society's Catalogue of Scientific Papers, a laborious task for which his accurate and varied knowledge gave him special qualification.

His death took place very suddenly as he was on his way home to Harrow after a day spent on his usual work at the Royal Society and the British Association. He knew practically everybody, and he gained the friendship and respect of all who knew him. In 1863 he married Harriet Dyke, second daughter of the late Arthur H. D. Troyle (formerly Acland), who, with four sons and five daughters, survives him.

SIR WILLIAM CHANDLER ROBERTS-AUSTEN, K.C.B., D.C.L.,  
D.Sc., F.R.S.

The Society has to record the loss of one of its most eminent members in Sir William Roberts-Austen, who died on November 22nd, at the age of 59. He was the son of George Roberts, and in 1885 assumed the name of Austen at the request of his uncle, Major Austen. He was educated at the Royal School of Mines,

and in 1865 became private assistant to the late Prof. Graham, the Master of the Mint. Since that time he has been continuously associated with Mint works, having been appointed "Chemist of the Mint" on the creation of the post in 1870, and Assayer in 1871. Additional duties were assigned to him in 1882, and in June last, on the death of the late Deputy Master, Sir William Roberts-Austen was appointed to fill the office *ad interim*. He was also Professor of Metallurgy of the Royal School of Mines from 1880 to the time of his death.

His early scientific work was mainly connected with the assay of gold and silver bullion, but from the year 1888 he devoted himself to the study of the physical properties of metals and alloys, and has been largely instrumental in building up the new branch of science to which the name "metallography" has been applied. He published an "Introduction to the Study of Metallurgy," and more than twenty papers describing original researches, some of the best known being as follows:—

"On the Liquation, Fusibility, and Density of the Alloys of Silver and Copper," 1875; "On the Mechanical Properties of Metals," 1888; "The Recording Pyrometer," 1891; "The Diffusion of Metals," Bakerian Lecture, 1896; and a series of Reports to the Alloys Research Committee of the Mechanical Engineers between 1891 and 1901.

As a lecturer Sir William Roberts-Austen had few equals, his five series of Cantor Lectures on Metals and Alloys at the Society of Arts, his Friday evening discourses at the Royal Institution, and his Presidential Addresses to the Iron and Steel Institute, being instances of his marvellous powers in arranging and polishing the wealth of material which always appeared to be at his command. He was one of the original members of the Physical Society, of which he was the first Secretary, and subsequently a Vice-President. He became a Fellow of the Royal Society in 1875, and served on the Council in 1890-2. He was a Vice-President of the Chemical Society, of the Society of Arts, and of the Institution of Mining and Metallurgy, an honorary member of the Institution of Civil Engineers and of the Institution of Mechanical Engineers, the President of the Chemical Section of the British Association in 1891, and one of the General Secretaries of the Association from 1897 to the year of his death. He was the President of the Iron and Steel Institute in 1899-1900.



He served on several Departmental and other Committees, his most noted services of this kind being those rendered to the Explosives Committee during the last two years of his life. He was made a C.B. in 1890, a K.C.B. in 1899, a D.C.L. of Durham University in 1897, and a D.Sc. of Victoria University. In 1890 he received the Order of the Legion of Honour from the French Government.

**JAMES WIMSHURST, F.R.S.**

Mr. Wimshurst was born on April 13th, 1832, and died suddenly of heart failure on January 2nd, 1903.

He was educated at Stelonheath House, London, and then served an apprenticeship at the "Thames Iron Works."

In 1853 he was appointed one of the Surveyors for Lloyds in London, and in 1865 was transferred to Liverpool, where shortly afterwards he took the position of Chief of the Registry. In 1875 he left Lloyds to become Principal Shipwright Surveyor to the Board of Trade, which post he held until he reached the age-limit in 1899.

His spare time he occupied in his own private laboratory, working along several mechanical and scientific lines, the most important of which was his work on Influence-Machines. A description of a Holz Machine, which he read in 1881, caused him to make first a small Holz, and then a large one having 12 revolving discs and 24 fixed glass inductor-plates. This machine he so improved as to make it certain that all the discs worked regularly with the same polarity. Following along this line of work, he next invented the machine which is now so famous under his name, and which has discs revolving in opposite directions but on fixed inductors. By careful thought and experiment he brought this form of machine to perfection, and made it far superior to all previous forms, especially in its ability to work under adverse atmospheric conditions, and to produce a continuous stream of electricity without reversing. This machine, as he made it, is invaluable for laboratory experiments, because it requires so little power and attention. It is also much used for Röntgen-ray work, and has lately been tried for the cure of Lupus.

Mr. Wimshurst was a member of the Institution of Electrical Engineers, and also a member of the Board of Managers of the

Royal Institution. In 1890 he was elected a Member of the Council of the Physical Society, and in 1898 a Fellow of the Royal Society. He freely gave all his scientific discoveries to the world, and many of his machines to friends and learned Societies. He was always glad to help a fellow-worker, and was a man of simple tastes and of a kindly genial nature. His loss is sincerely felt by all who knew him, and by the Fellows of this Society in particular.

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## ADDRESS OF THE PRESIDENT,

Dr. R. T. GLAZEBROOK, F.R.S.

*Delivered at the Annual General Meeting,  
February 13th, 1903.*

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My first duty as it is my pleasure on taking this Chair is to thank the Members of the Society for placing me in it.

I accept the position as a recognition of the importance of the post I hold, and a token of their confidence and expectation that the National Physical Laboratory will become a great factor in promoting the progress of Physical Science. This it is the object of our Society to further.

Whether it is doing this as successfully as it might, is a question to which we may perhaps return. Meanwhile, let me occupy you for a few minutes with a reference to some of the events since our last Annual Meeting.

We are poorer, for the hand of death has been laid on not a few who have for years been among our honoured Members. Gladstone and Roberts Austen, Griffith and Wimbushurst have each contributed in no small degree to the advance of natural knowledge.

Dr. GLADSTONE was our first President, a very perfect gentleman, who devoted himself with untiring energy, through many years of active life, to promoting the good of his fellows. Most of his work perhaps was of special interest to the chemist rather than to the physicist, but his long series of experiments on molecular refraction, and some of his studies on the chemical action in a cell, have earned him a high position among physicists.

ROBERTS AUSTEN was our first Secretary, and in its early days, now nineteen years ago, the Society owed much to his tact and to his enthusiasm. In late years his increasing duties had prevented any frequent attendance at our meetings; when he came, the contributions he made to our discussions were always welcome.

His name will live in the work of the Alloys Research Committee of the Institution of Mechanical Engineers, and in the long series of Reports he issued for that Committee.

GEORGE GRIFFITHS was not the author of any notable paper or discovery, but by the ability with which he discharged the duties of his official position as Secretary of the British Association, he contributed in no small degree to the advance of science. His knowledge too of the literature of our subject was unrivalled. Many of us have profited from time to time by his generous help when struggling to find out what had been done in some subject of enquiry.

JAMES WIMSHURST freely gave to science the results of those ideas which his skill and practical training enabled him to work out in so perfect a form.

These four men have all held office in our Society, and in their several ways helped to promote its prosperity.

The Report of the Council mentions other familiar names of men who are no longer with us, and among them two of our distinguished Honorary Fellows, Ricardo Felici of Spezia, and Alfred Cornu of Paris.

To myself FELICI is known by the beautiful series of experiments published in 1852 and 1859, by which he established the fundamental laws of electromagnetic induction. Those who do not know his work, now fifty years old, let me recommend to read Maxwell's account of it (Maxwell, *Electricity*, vol. ii. § 536-539).

Maxwell concludes thus:—"These experiments therefore show that the total current of induction depends on the change which takes place in a certain quantity  $M\gamma$ , and that this change may arise either from a variation of the primary current  $\gamma$  or from any motion in the primary or secondary current which may alter  $M$ ."

This law now enters so largely into our daily life and appears so old, that it may seem strange to realize that the man by whose work it was first completely established, died but yesterday, and was an Honorary Fellow of our Society. It is a pleasure to us to know that he attached a high value to that membership.

ALFRED CORNU's name is perhaps more familiar. Some of us knew him well and valued his friendship no less than we admired his work.

The perfection of his style, his skill as an experimenter, and his personal charms all contributed to make him deservedly esteemed.

It is but a few years since we heard him express in the Rede Lecture at Cambridge, in terms most happy and appropriate, those sentiments of admiration and respect which all men of science felt for that great Cambridge Physicist, who only last week was laid to his rest.

GEORGE GABRIEL STOKES it seems was not a Fellow of the Society. We are the poorer for it, and regret it. To many here I suppose he was hardly known, even by sight. To myself, for nearly thirty years he has been a most kind master and a friend; my first research was due to his inspiration, he lent me the apparatus to carry it out, and encouraged me by his advice and help during its progress.

He was the greatest of those who, since Newton's day, have sat in Newton's Chair; it would be a fitting task for the Physical Society to take its share in raising for him a monument near that of Newton in the Abbey.

To turn now for a moment to the more domestic affairs of the Society.

We have today suffered a heavy loss by Mr. Elder's retirement from the post of Secretary. The Council accepted his resignation with regret, but the reasons he gave for wishing to retire could not be gainsaid.

You will feel that ten years of devoted service have earned your hearty thanks. In your name I feel sure I may express the hope that Mr. Elder may be long able to help us by his advice and counsels.

Many years ago when he was my pupil, I learned to value his cooperation, and my own task as your President would seem a less responsible one, if I could have the assurance that the business affairs of the Society were still in his experienced hands.

At the same time, I am confident that the choice of a successor has been a wise one, and that in Mr. Cooper you have found an officer who has both the will and the power to further the interests of physical science, the object which unites us all.

How best can we do this? The Society has had a distinguished

history, its publications have a real value, in particular the re-publication of certain Memoirs and the initiation of 'Science Abstracts' will be of permanent service to the world.

'Science Abstracts' this year enters on a new period of its career, which promises for it a wider sphere of usefulness and a larger growth. I trust that you will feel the Council have acted wisely in the arrangements they have made.

But withal it can hardly be urged that the growth of the Society has been commensurate with the interest and importance of the subject.

Of late years our numbers have been nearly stationary, and a Society which does not grow, stagnates and will die. Is our utility at an end? Have we fulfilled our appointed task, and must we make way for those more technical Societies which flourish so abundantly? I would say no! Rather let us profit by their example, and claim for ourselves a new and a wider range of activity.

Physics is a far-reaching subject, one which has contact at many points with other sciences, and our range of papers should be correspondingly great.

And yet of recent years, at least, the range has narrowed. There is an ill-defined feeling that we do not deal in so-called technical papers. The feeling is mistaken, I think. There are some technical papers, it is true, which are better absent—for example, a paper in which the author describes some apparatus or instrument he has patented, not because of its scientific merit, but because he wishes to advertise his patent; but what, for example, are the technical applications of electricity but applied physics.

Not a few of the papers which have recently been read before the Institution of Electrical Engineers—I know the President of the Institution agrees with me in this—might at least as well, probably better, have been read before us.

I need only mention two in the present Session: Dr. Fleming's most interesting and important paper on Photometry, which contains, besides details of the photometry of electric lamps, a valuable discussion of principles reaching beyond the domain of the Electrician; and the discussion on the Metric system, opened recently by Mr. Siemens and Sir Frederick Bramwell.

Or again, the Electrochemists have recently formed themselves into a Society. I believe it was inevitable; there must be number of points of detail which can best be discussed by a body of experts

among themselves, and we are not all experts in Electrochemistry. Nevertheless, I am sure there are numberless matters dealing with Electrochemistry which may well be brought before us, and on which, if proper preparation is made, discussion by a mixed audience may throw a useful light. Take for example the very interesting paper by Dr. Inglis read in November last. And moreover, of how great interest to a student of physical theory are the points which rise in practice. Prudence forbids me to touch on one subject recently the cause of vigorous discussion, but its interest cannot be denied.

Let me refer to another closely allied to it, on which I have been asked some questions, which I could not answer—the thermodynamics of the petrol motor; or to a third, the optics of the photographic lens.

I trust sincerely that, at any rate while I hold the office of President, no one will be deterred from bringing forward papers on such subjects, because he thinks them too technical. We should be prepared, that goes without saying, to discuss difficult points of theory; at the same time, it is our bounden duty to bring our knowledge of physical facts and laws to bear on the every-day life of the nation, and to make our influence as a corporate body felt in its counsels and its life.

But if we are to do this; if our debates are to be interesting and real, care and preparation are required.

We have a custom, I do not think it is a rule, to print any important paper either in full or in abstract before it is read. Now I have been too long a secretary of a scientific society not to know the difficulty of enforcing this. It can only be done with the cordial concurrence of the senior and more influential members; but in the case of any paper worth discussing, it is essential that the custom should become a rule, and that proofs should be in the hands of those who may be expected to discuss the paper some days at least before the meeting. Nor is this in itself enough; persons who might contribute to the discussion must be asked to come and take their part. It might be convenient, I think it is done elsewhere, for the officers to divide the list into groups of persons who might be regarded as specialists in the various branches of physics, so as to be ready to send out notes asking for assistance in a discussion easily and readily. I recommend the suggestion to our Junior Secretary, who has, I think, some such scheme in his head; we should then avoid the catastrophe

which happened not long since, when a distinguished Fellow brought forward an intricate paper on a difficult subject. None had seen it, and it passed almost without discussion.

Again, we might arouse interest by arranging at times for set discussions. I should myself like to see this more generally done.

One obvious source of weakness is the fact that we have no home of our own. Our hosts here are very kind to us, but a hired lodging is not a home. We have no place to collect the belongings of the Society; our books are at South Kensington. Does anyone find them useful? When a Fellow wishes to illustrate his paper by experiment, all the material has to be collected from afar; the opportunities for meeting are but few; corporate life as a Society is entirely wanting. I do not know that I can suggest any method of remedying this at present, but it is to be borne in mind.

Then as to the hour of meeting. Most of us are busy men, and at 5 p.m. have done a good day's work; when we are tired and want our tea and rest, we have to come here to discuss Physics.

It is true we have an illustrious example next door, but, speaking for myself, I must say I think it is the half hour before the meeting that is of value at the Royal Society.

There are of course difficulties in arranging for an evening meeting, and I do not wish to be understood as pressing a change; it is, however, a matter on which I should like to take the opinion of the Society, and I trust it may be possible during the ensuing year to discuss it.

The Technical Societies could not meet in the daytime, their members are otherwise engaged. I want the Physical Society to appeal to the same class of men, and not merely to teachers and lecturers in Physics who are resident in London.

Another suggestion for increasing our usefulness was made to me the other day. I put it forward merely for discussion, the difficulties of giving it effect are great, yet if it could be done it would be of value.

It was pointed out to me that there are men in isolated positions about the country who are interested in Physics and have some small opportunities for research, but have no one to guide them. Occasionally, such a man may attempt, for a time, to work at some problem only to find that he has been forestalled, or possibly



that the problem is insoluble; in other cases he does not know where or how to start. Would it be possible to formulate, for the guidance of such would-be workers, a list of problems they might attack, indicating in a general way the methods of approach. The value of such a list is obvious, I am not sure that it is feasible.

Other suggestions may be made with the object of increasing our utility and our strength; it will be for the Council to consider these and to bring the result of its deliberations before you in due time.

*Theoretical Optics since 1840.—A Survey.*

Sir George Stokes took his degree in 1841; the first of the papers contained in his Collected Works was read in 1842: he became Lucasian Professor in 1849.

Speaking as I do so soon after his death, it is, perhaps, not unnatural to look back over the progress of our Science during the sixty years for which he has been one of the most prominent of its exponents.

To attempt such a task in any completeness would need a fuller knowledge and an abler pen than mine; will you, however, bear with me if I take one corner of the field covered by his activities and attempt a brief survey of this. It is, perhaps, the more necessary, for I think it is not always recognized how much of our knowledge of Optical Science is due to Stokes. It was he who first verified with any degree of exactness Huyghens' construction for the refraction of light at a uniaxial crystal; the interpretation of Kirchhoff's discovery of the coincidence between the dark lines of the solar spectrum and the bright lines of certain incandescent solids and gases is due to him, and on this the whole of spectrum analysis rests; he explained the phenomena of fluorescence, and as an old man, some years ago, expounded in his own unrivalled manner the origin of the Röntgen rays and their connexion with the kathode rays. The analysis of a plane wave of light into its constituent parts, and the first dynamical account of diffraction, are due to him; and his experiments, if we accept any modification of the elastic-solid theory of light as true, settled that Fresnel's explanation of the cause of refraction, rather than that of Neumann and MacCullagh, is the right one.

In his brilliant Rede Lecture, Cornu writes:—

“The study of the properties of waves, looked at from every aspect, is then at present the really fruitful path.

“It is that which Stokes, in his double capacity of mathematician and physicist, has followed.... All his beautiful investigations, whether in hydrodynamics or in theoretical or experimental optics, relate to the transformations which waves undergo in the diverse media through which they pass.

“In the varied phenomena which he has discovered or analysed, movement of fluids, diffraction, interference, fluorescence, Röntgen rays, this guiding idea that I have pointed out is ever visible, and it is this which has made the scientific life of Sir George Stokes one harmonious whole.”

Let us consider then very briefly the progress of theoretical optics since the days of Stokes' first paper on the subject: “On the Theories of the Internal Friction of Fluids in Motion, and of the Equilibrium and Motion of Elastic Solids”\*. The advance in the early part of the century had been most marked. The discovery of the principle of interference by Young, and the brilliant work of Augustin Fresnel, who had covered the ground with giant strides, had placed the undulatory theory on a firm footing, but there was no consistent view of the subject which would account even for the facts then known on a rational basis.

Fresnel's theory of double refraction was not dynamical; he arrived at it in the first place by purely geometrical reasoning, based on Huyghens' construction, and only attempted at a later date to give it a mechanical basis. In this attempt he failed. “If we reflect,” says Stokes, “on the state of the subject as Fresnel found it and as he left it, the wonder is not that he failed to give a rigorous dynamical theory, but that a single mind was capable of effecting so much.”

Between the days of Fresnel and Stokes great men had worked at the subject. Navier, Poisson, and Cauchy in France; Neumann in Germany; MacCullagh in Dublin; and George Green in Cambridge, had all contributed their share, and the results were somewhat confusing.

MacCullagh and Neumann, treating the æther as an elastic solid, had obtained on certain hypotheses Fresnel's laws for reflexion and refraction, and his theory of double refraction.

\* Camb. Phil. Trans. viii. (1845).

Green, using a somewhat different method, had shown, apparently, that the tangent law was only an approximation to the truth, while the wave-surface could only be deduced from the true equations of an ælotropic elastic solid by some forced and improbable relations between the constants.

According to all the theories, two waves in general can traverse an elastic medium, the one travelling with velocity  $\sqrt{A/\rho}$ , the other with velocity  $\sqrt{B/\rho}$ , where  $A$  and  $B$  are two constants. Of these the first consists of longitudinal, the second of transverse vibrations; and since there is no evidence of the former wave in optics, the constant  $A$  must either vanish or be infinite.

Neumann's theory assumed  $A$  to vanish; Green had shown that for an elastic solid with free boundaries the condition of stability demanded that  $A - 4/3 B$  should be positive, and hence he assumed  $A$  to be infinite. On this view of the æther he was clearly right. Such was the position of the problem in 1839, the year in which the papers of Green, MacCullagh, and Cauchy were published. Stokes' earliest paper on the subject, written when he was 26 years old, deals with the properties which we must assign to the æther if we are to explain the facts observed. To propagate transverse waves it must behave to light motions as an elastic solid; the constancy of the length of the year, and other astronomical results, shows that it opposes no sensible resistance to the motion of the earth and the planets, for such motions it has the properties of a perfect fluid.

He distinguishes—the fact is well-known now, but it was a great step then—between the two kinds of elasticity, rigidity and resistance to compression.  $B$  is a measure of the rigidity,  $A - 4B/3$  of the resistance to compression. For a fluid, then, which is practically incompressible, the ratio of  $A$  to  $B$  may be very great, as Green requires it, while in Stokes' view it is still possible that for the tiny motions involved in the propagation of light the fluid may have rigidity.

However, be this satisfactory or not, and the difficulty is one which occurs in every elastic-solid theory of Optics, the result remains that an elastic-solid theory is not consistent with the facts. The phenomena of reflexion and refraction at the bounding surface of two media may be due either to a change in density or to a change in rigidity.

Green's theory of refraction assumes the change to be one of density, the rigidity of the æther in all isotropic media is the

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same; his theory of double refraction assumes this to arise from a variation of the rigidity in different directions within a crystal.

These difficulties are clearly exposed in Stokes' Report to the British Association in 1862, in which he also shows that MacCullagh and Neumann's theory is impossible so long as the potential energy of the æther when transmitting light is assumed to be that of a strained elastic solid. If we suppose the æther to differ from an ordinary elastic solid but to possess what has been called rotational elasticity, in consequence of which it opposes forces tending to cause molecular twist to an extent proportional to the twist, then MacCullagh's form of the potential energy is obtained and his conclusions hold. From this point of view the matter has been developed of late years by Larmor.

The Report of 1862 deals with another matter, specially interesting to myself, because in later years Stokes encouraged me to pursue it.

Up to that date the experiments to verify Huyghens' construction for a uniaxial crystal had been of the roughest character. Stokes devised a method of testing the construction to a very high degree of accuracy and carried it into effect for Iceland spar. The results are very briefly referred to; they were published later, but hardly in greater detail, at Lord Kelvin's urgent request, in the Proceedings of the Royal Society.

The outcome was that while for a uniaxial crystal at least Huyghens' construction was undoubtedly true, no theoretical basis could be given for it.

It was left to Maxwell to carry the question a stage further. He showed that the laws which regulate the propagation of electric force in a crystal are identical with those of light, while experiment proved that the velocity of light is the same as that of an electric disturbance, and hence we have the electromagnetic theory of light.

It should be noted, however, that this theory, as Maxwell left it, is not mechanical. Electric displacement and magnetic force are vector quantities which accompany each other in a changing electric field. They satisfy certain equations; and it follows from these, and the result is verified by experiment, that they are propagated according to the same laws as light. It is reasonable to suppose that the periodic disturbance which constitutes light is very intimately connected with one or other of these; the supposition that it is identical with Maxwell's electric displacement leads to consequences consistent with fact, and, indeed, in the able hands

of those who have developed the theory has been the fruitful means of correlating many varied phenomena; but it does not tell us what electric displacement is, or how it is related to the movements of the æther; neither does it enlighten us as to the structure and mechanical properties of the æther, beyond the simple fact that in the æther transverse waves only are propagated, no forces can be called into play which tend to set up a pressural wave. Maxwell himself attempted to formulate a mechanical model of the æther, and to some extent succeeded. Lord Kelvin, so fertile in his thoughts, has made various suggestions: we will return to one later. To-day the electron theory of electricity, thanks mainly to the brilliant work of Stokes' Cambridge colleague, J. J. Thomson, holds the field; but the relation of the electron to the æther and the mechanism by which electrons produce æther waves have yet to be discovered.

Larmor's suggestion that the flow of æther constitutes magnetic force, while a twist in an æther endowed with rotational elasticity produces electric displacement, forms perhaps the most consistent picture of the process which we possess.

Lord Kelvin, indeed, in 1888, suggested a structure for the æther which allows of a homogeneous mechanical account of optical phenomena being given.

On this view the resistance to compression of the æther is negative, if free it would collapse, but the necessary stability is given by the supposition that it is fixed at the boundaries; it is a structure like a collection of soap-films stretched across a wire framework; if the connexion be broken the whole collapses, so long as it remains the system can propagate transverse waves. With such an æther there is no difficulty in giving a consistent account of Optics, but it is difficult to imagine that the æther has such properties. I believe, however, that Lord Kelvin now thinks that a slight modification of his original hypothesis will lead to the same result so far as optics are concerned, but will enable him to get over the difficulty of postulating fixed boundaries.

On such an hypothesis the molecular velocity of the æther might measure magnetic force, while electric displacement would then be proportional to the curl of the twist; or we might adopt the analogy suggested by Heaviside ('Electrician,' Jan. 23, 1891), and developed, as I have said, by Larmor, according to which the kinetic energy measures the magnetic force and the twist the electric displacement.

The electromagnetic theory, though it does not rest on a mechanical basis, has linked together optical and other phenomena in a striking fashion. The advance from the days of Green has been a great one.

And leaving now the general theory, the development of its details has not been less striking. On all sides there has been advance, and along most of the lines of advance Stokes was a pioneer.

Newton's difficulty in accepting the undulatory theory was really solved when Young enunciated the principle of interference, but it needed Fresnel's experiments to convince men of its truth. It was clear, of course, that the effect at any point due to a wave of light could be calculated by finding the effect due to each element of the wave and summing these; but Stokes, in his papers on diffraction (1851), was the first to establish a correct expression for the effect produced at a distant point by an element of the wave and to show how these effects were to be summed.

The germ of all that has been discovered by means of spectrum analysis is contained in his explanation of Kirchhoff's original experiment, often quoted by Lord Kelvin, and from his paper on "Fluorescence" have sprung the modern theories of dispersion, including anomalous dispersion. On this point the note he has added to this paper in the third volume of his Collected Works has a special interest. Although he did not fathom the connexion between æther and matter, and, on the whole, the criticisms passed by later writers on his theory of aberration are to be accepted as justified, his papers must be studied by any one who is anxious to penetrate the mystery, and did much to put the facts in a clear light.

My survey is, I realize, entirely inadequate; it is but a fraction even of the corner of the field I set out to examine that I have covered, but I must stop. I have said enough, I hope, to show that progress has been continuous and marked, and in no small degree that progress has been due to the work of Sir George Stokes.

I had intended to bring before you some more practical questions connected with the work of my own Laboratory. These must await a more fitting opportunity; meanwhile let me conclude as I began, by thanking you very heartily for placing me in this position, and assuring you of my desire to forward your best interests.



